CHAPTER 1

THE SCHMIDT REACTION

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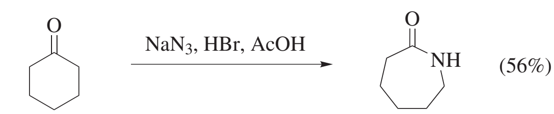
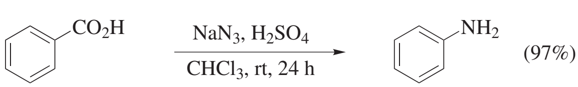
INTRODUCTION

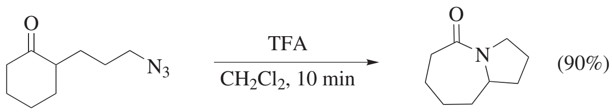
The term “Schmidt reaction” describes a family of related reactions that use hydrazoic acid or an alkyl azide to react with an electrophile. A few representative examples are depicted in Eqs. 1–3.[1–3] Depending on the reactants employed, the product of the reaction can contain an amide or a number of related functional groups (Fig. 1). Despite this diversity, all Schmidt reactions have the characteristic of incorporating nitrogen into the product and it is this feature that has placed this chemistry among the most useful means for the synthesis of nitrogenous compounds.



(Eq. 1)



(Eq. 2)



(Eq. 3)

The Schmidt reaction was first reported in 1924 by K. F. Schmidt,[4] but came into its own in the 1940's and 1950's, largely through the efforts of P. A. S. Smith[1,5–8] and L. H. Briggs.[9,10] The classical Schmidt reactions, defined as those that specifically employ hydrazoic acid as the azide component, are the subject of an earlier *Organic Reactions* chapter.[11] In addition, extensive review literature exists on the subject.[12–20]

The most commonly used variant of the Schmidt reaction is the reaction of a ketone or aldehyde with hydrazoic acid to afford an amide. These reactions usually employ a stronger protic acid to enhance the reactivity of the carbonyl group. Cyclic ketones afford lactams that contain one additional ring atom relative to the starting material. The utility of this reaction is heightened by the availability

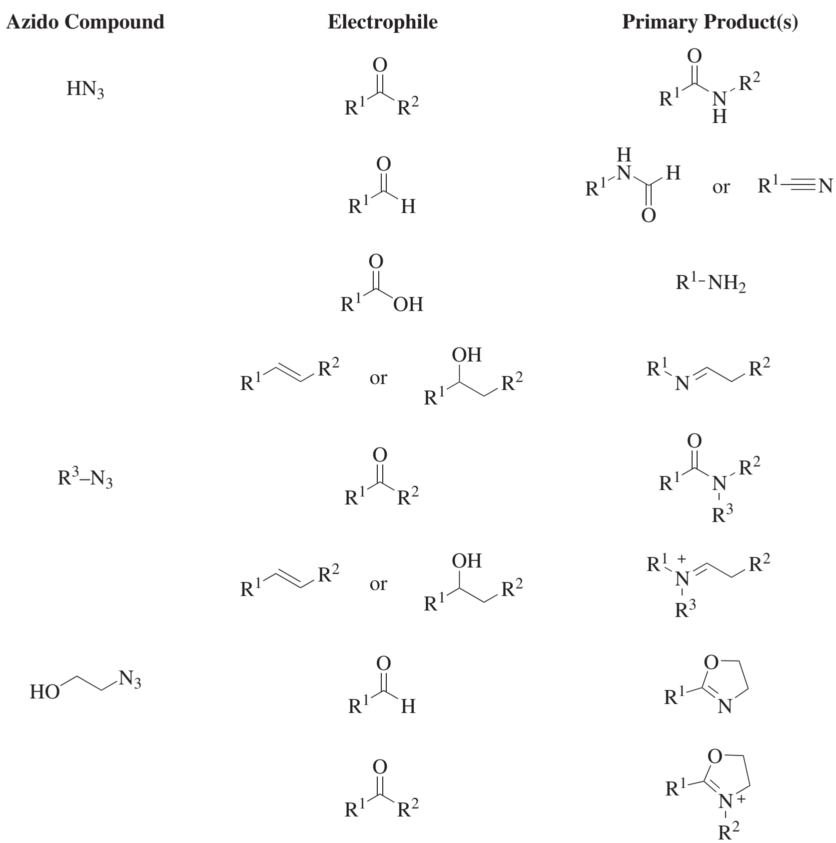


Figure 1. The family of Schmidt reactions.

of an essentially limitless number of ketones and by the ready reduction of the amide carbonyl group to afford the corresponding amino compound. In addition, most Schmidt reactions of this type occur with predictable (if not fully selective) site selectivity and stereoselectivity.

Hydrazoic acid also reacts with related species such as carboxylic acids and carbocations derived from alcohols or alkenes. The identification of all of these processes as variants of the Schmidt reaction is due to their common mechanistic features, involving first, the nucleophilic addition of hydrazoic acid to the reactive electrophile and, second, the rearrangement of this unstable adduct to afford the product. The loss of molecular nitrogen during the second stage of these reactions provides a powerful driving force for conversion into product. The mechanistic variations among classes are discussed in the appropriate sections.

The superficial similarity of alkyl azides to hydrazoic acid, entailing only the replacement of the proton in HN_3 with an alkyl group, immediately suggests that azides should undergo their own Schmidt reactions when encountering an electrophilic species. In the 1950's, Boyer reported a limited series of successful reactions of alkyl azides with aromatic aldehydes to afford amides.[21] In the 1990's, it was reported that Lewis acids could effect the addition of azides to ketones and also that azides were facile partners in Schmidt reactions of carbocations, thus opening the door to the direct synthesis of *N*-alkylated amides from ketones[3,22] or tertiary amines from cations derived from alcohols or alkenes.[23,24] Simultaneously, it was recognized that intramolecular variants of these reactions can provide routes to multicyclic nitrogen heterocycles.[3,23]

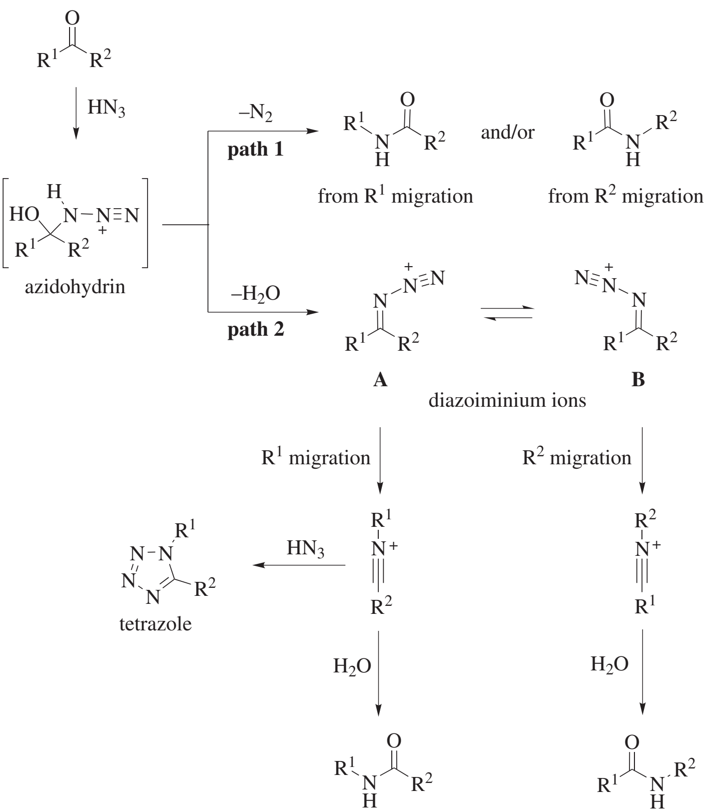
This chapter will discuss progress in all of the above classes of reactions, with the main restriction that only examples not included in the 1946 edition of *Organic Reactions*[11] will appear in the tables, ending with references published through the end of 2009.

MECHANISM AND STEREOCHEMISTRY

All Schmidt reactions involve the initial nucleophilic attack of hydrazoic acid or a related azide species onto an electrophile. Although the latter is most commonly a carbonyl group activated by a protic or Lewis acid, the electrophile can also be either a stabilized or unstabilized carbocation. The greatest mechanistic diversity through the class arises from the ultimate fate of the intermediate formed in this initial step. Every one of these reactions is driven by the loss of molecular nitrogen en route to its nitrogen-containing product. Each of the different classes of Schmidt reactions will be considered separately.

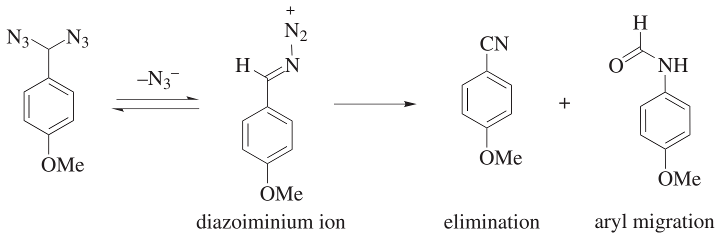
Reactions of Hydrazoic Acid with Ketones

The most heavily studied variant of the Schmidt reaction is that of a ketone with hydrazoic acid (Scheme 1). This reaction begins with the addition of HN_3 to the protonated carbonyl group to afford an azidohydrin intermediate. At this stage, the reaction can proceed via one of two principal routes. In path 1, rearrangement of the azidohydrin intermediate directly affords an amide via a mechanism related to that of the Baeyer–Villiger reaction.[25] Alternatively, path 2 involves elimination of water to afford a diazoiminium species, which can subsequently rearrange to form an iminium ion that must be hydrated to give the final product (analogous to the commonly accepted mechanism of the Beckmann rearrangement).



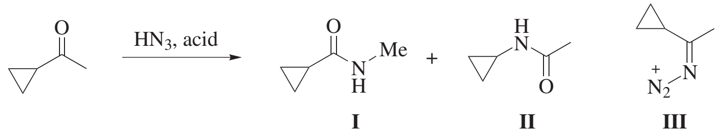
Scheme 1

The Beckmann mechanism was originally proposed by Smith[1] and, although the subject of considerable spirited discussion over the years, this mechanism is still favored by most authors. The main reasons are (1) the correlation of the migrating group with size, which is consistent with formation of the least sterically encumbered diazoiminium ion and antiperiplanar migration (also seen in the Beckmann rearrangement); and (2) the fact that tetrazoles are common byproducts of the Schmidt reaction, and form in increasing amounts when high concentrations of hydrazoic acid are present. The diazoiminium ion generated in the absence of water from the diazidoalkyl species shown in Eq. 4 gives the Schmidt reaction product; in this case, both elimination to nitrile (typical of Schmidt reactions of aldehydes) and aryl migration are noted.[26,27] Parenthetically, a protonated gem-diazide has been suggested as a possible intermediate in some Schmidt reactions.[28] Although this work proves that diazoiminium ions are possible intermediates in the reaction, it is difficult to establish the *required* involvement of such species.



(Eq. 4)

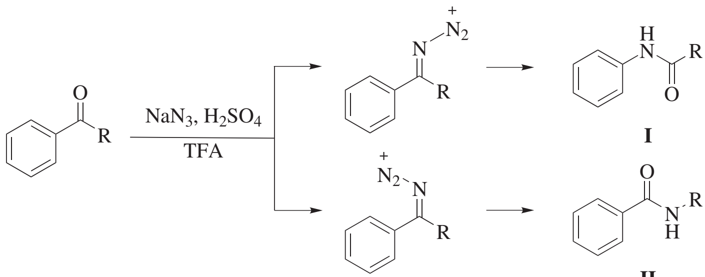
The demonstration of successful Schmidt reactions of alkyl azides clearly removes any objection to a mechanism involving direct azidohydrin rearrangement.[3,22,29] Thus, despite the general acceptance of the Beckmann mechanism, it has been suggested that the Baeyer–Villiger mechanism can operate under certain conditions. For example, Shechter has suggested that the mechanism of the Schmidt reaction of cyclopropyl ketones depends in part on the acid strength of the reaction medium (Eq. 5).[30,31] However, alternative explanations, such as the preferential formation of stereoisomeric intermediate **III** in 50% sulfuric acid, cannot be totally ruled out.



(Eq. 5)

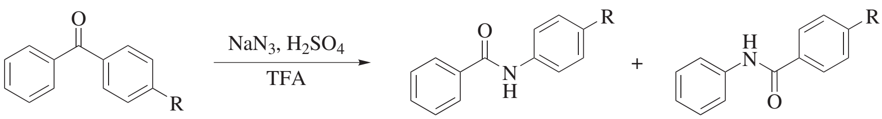
89% H_2SO_4, **I** + **II** (88–100%) **I**:**II** = 27:73
50% H_2SO_4, **I** + **II** (88–100%) **I**:**II** = 90:10

Under the Beckmann mechanism, stereoelectronic effects determine which group undergoes migration. In a systematic examination of a series of phenyl ketones containing increasingly larger alkyl substituents, the product ratio correspondingly favors alkyl group migration (Scheme 2).[6] These results are consistent with the hypothesis that the ratio of the intermediate diazoiminium ions, coupled with the synchronous and antiperiplanar migration of the carbon to the electron-deficient nitrogen, determines the site selectivity. An important proviso is that theoretical calculations suggest a high barrier for direct interconversion of the diazoiminium ions.[32] However, intermediates leading to **A** or **B** (Scheme 1) can interconvert via reversible addition of water under the reaction conditions (i.e., by reversion to the azidohydrin and subsequent dehydration); it is also possible that their ratio is kinetically controlled. An analogous study of substituted benzophenones does not belie any clear dependence of migrating group selectivity on the electronic nature of the aromatic rings, suggesting that "migratory aptitude" does not play a strong role in determining the site selectivity in these particular reactions (Eq. 6).[7]



R	Yield (%) I + II	I:II
Me	81	95:5
Et	80	85:15
i-Pr	57	51:49
t-Bu	—	0:100

Scheme 2

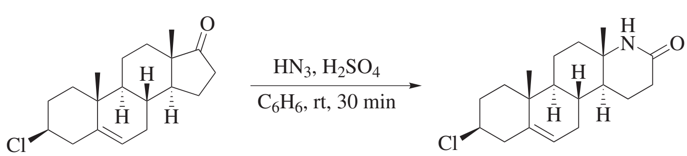


I I + II (—) II

R	I:II
O_2N	51:49
Cl	59:41
Me	54:46
Ph	52:48
MeO	61:39

(Eq. 6)

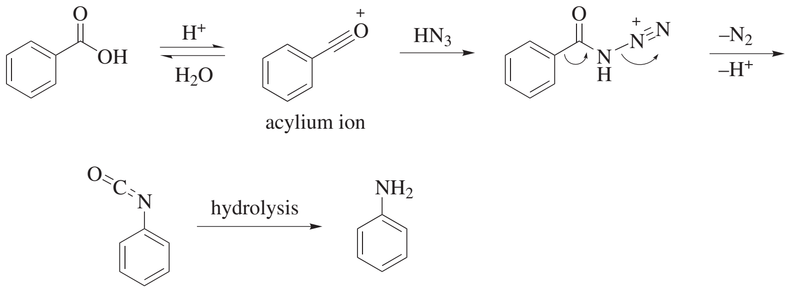
An important feature of the Schmidt reaction is that a stereogenic carbon migrates with retention of configuration. This behavior is consistent with related processes such as the Beckmann[33] and Baeyer–Villiger[25] reactions and extends throughout the entire family of Schmidt reactions. The reaction of the steroidal ketone shown in Eq. 7 is typical; for an acyclic example, see Eq. 60 in the "Applications to Synthesis" section.[34]



(60%) (Eq. 7)

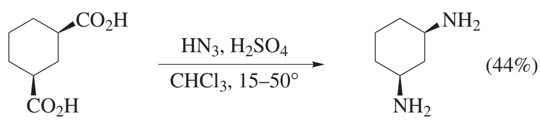
Reactions of Hydrazoic Acid with Carboxylic Acids and Aldehydes

These variants of the Schmidt reaction are mechanistically less ambigious. The reactions of carboxylic acids with hydrazoic acid uniformly afford amines as there is only the possibility of migration of a single group in an acyl azide intermediate. In these cases, the primary product formed following alkyl or aryl group migration is an isocyanate. Addition of water followed by loss of carbon dioxide leads to the final product, an amine (Scheme 3).

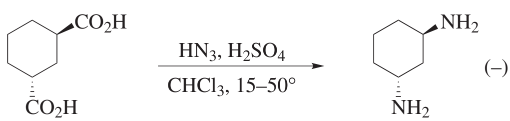


Scheme 3

The reactions of carboxylic acids with hydrazoic acid permit the stereospecific synthesis of amines via migration of a stereogenic carbon with retention of configuration (Eqs. 8 and 9).[35]

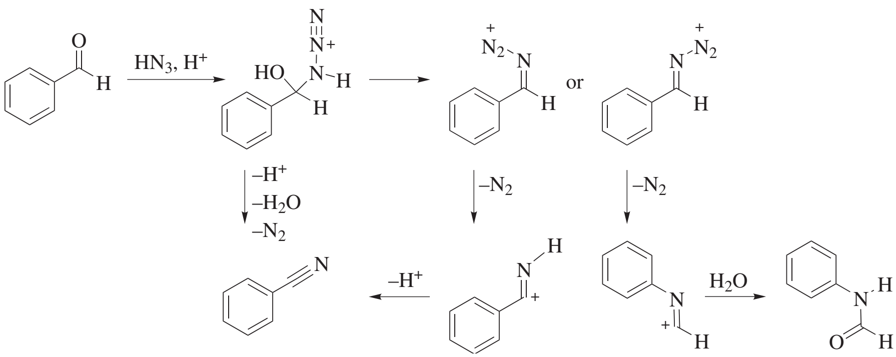


(Eq. 8)



(Eq. 9)

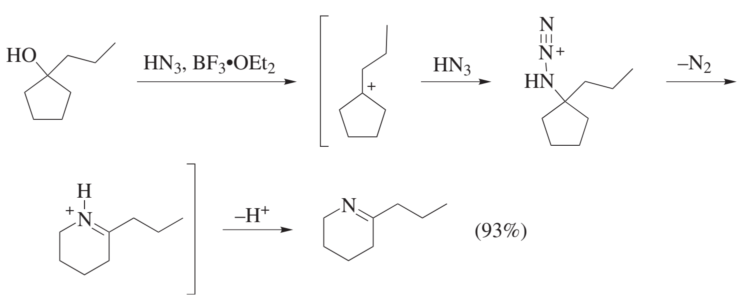
The mechanism of the reaction of hydrazoic acid with an aldehyde has not been fully established, partly because this variant of the Schmidt reaction is not as useful as others and therefore little work has been devoted to understanding it. These reactions are believed to occur via the Beckmann mechanism, affording first a diazoiminium ion that can rearrange via migration of an aryl or alkyl group to ultimately afford a formamide derivative upon hydration and tautomerization. However, the predominant product of this reaction is usually a nitrile (Scheme 4). One mechanism for the formation of a nitrile requires the intermediacy of the sterically unfavorable diazoiminium ion; however, this isomer may be kinetically favored.[36] Formation of the nitrile from this intermediate occurs by either hydride migration followed by proton elimination or concerted elimination. An alternative proposed mechanism is that the unprotonated version of the azidohydrin intermediate is converted into the nitrile (by an unspecified series of steps), whereas the formamide product arises from the diazoiminium ion as shown (Scheme 4).[37,38] This proposed mechanism is based in part on the observation of overall second-order kinetics and on the dependence of product ratio on acid strength.[37,38]



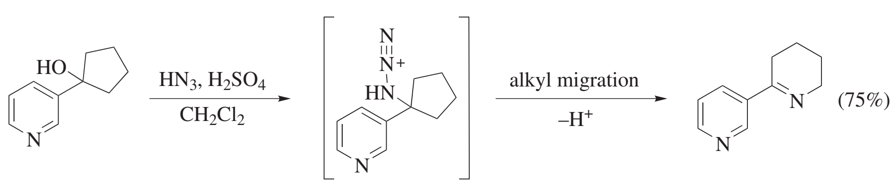
Scheme 4

Reactions of Hydrazoic Acid with Carbocations Derived from Alkenes or Alcohols

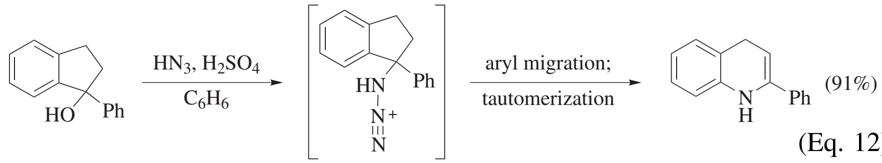
The reactions of hydrazoic acid with carbocationic species generated from alcohols or alkenes afford imines that result from nucleophilic addition of hydrazoic acid to the cation followed by alkyl or aryl group migration (Eqs. 10[39] and 11[40]). For cyclic compounds, imines are the usual reaction products, but tautomerization to the corresponding enamine is possible (Eq. 12).[41]



(Eq. 10)

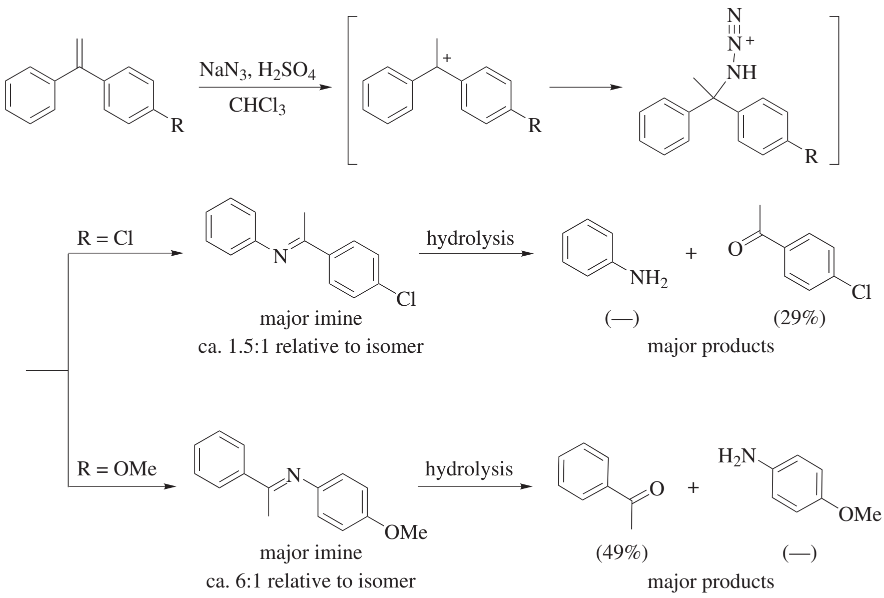


(Eq. 11)



(Eq. 12)

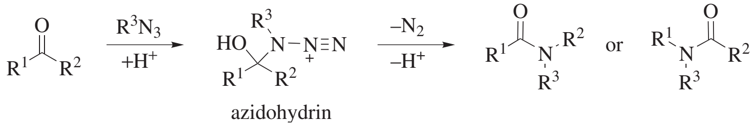
Also possible, and often observed in acyclic substrates, is hydrolysis of the imine to an amine and a carbonyl compound. Migratory aptitude likely plays a role in determining the site selectivity of the migration step due to the lack of a stereochemically defined diazoiminium intermediate in the reaction (Scheme 5).[42]



Scheme 5

Reactions of Alkyl Azides and Hydroxyalkyl Azides with Electrophiles

The discovery that alkyl azides react with various electrophiles[3,21,23] expands the scope of the Schmidt reaction and adds to the understanding of its mechanism. Specifically, because the adduct of an alkyl azide and a ketone is very unlikely to undergo loss of water to afford a diazoiminium ion containing adjacent positive charges, the competency of the initially formed azidohydrin species to directly afford an amide is generally viewed as unambiguously established. This reaction proceeds in both the intermolecular sense (Eq. 13)[22] and also when the azide is covalently attached to the ketone (Eq. 14).[3]

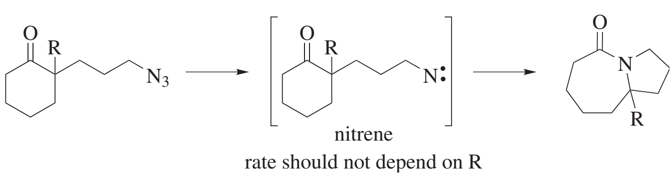


(Eq. 13)

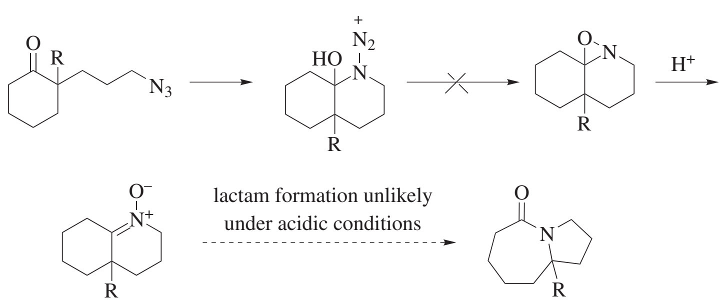
(Eq. 14)

R = H, 10 min (83%)
R = CO_2Me, 10 min, >90% recovered starting material
R = CO_2Me, 16 h (66%)

The possible involvement of nitrene intermediates is ruled out by comparing the rates of reactions of electronically disparate ketones. Whereas 2-(3-azidopropyl)cyclopentanone undergoes complete reaction in trifluoroacetic acid within 10 minutes at room temperature, similar treatment of an analog containing a 2-carbomethoxy group does not give significant conversion (Eq. 14).[3] However, it is possible to achieve a 66% yield of the lactam upon extended exposure to trifluoroacetic acid. It would be extremely unlikely that the rate of decomposition to a nitrene would be affected by the presence of a distant ester group (Eq. 15). In addition, the recovery of intact ester-substituted azide under conditions sufficient for the complete reaction of the unsubstituted version rules out nitrene intervention in at least the intramolecular reaction. Another unlikely mechanism is conversion of an azidohydrin to an oxaziridine via O–N bond formation (Eq. 16). Although oxaziridines can undergo thermal rearrangements to lactams,[43] they rearrange under acidic conditions to afford nitrones rather than amides.[44] Neither oxaziridines nor nitrones have ever been reported as products from the reactions of azides and carbonyl compounds.

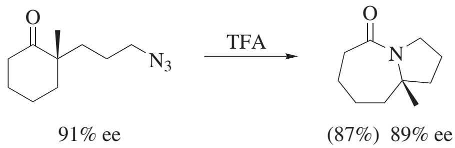


(Eq. 15)



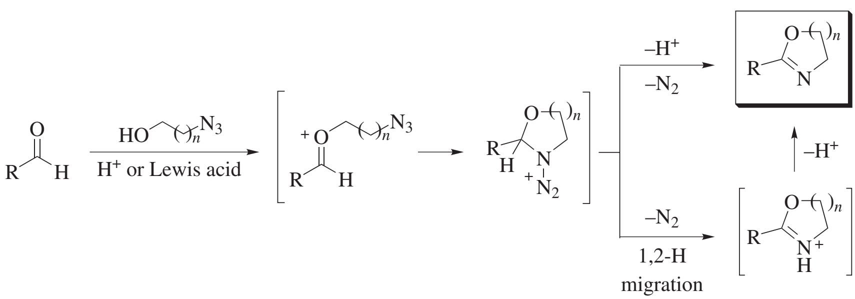
(Eq. 16)

The intramolecular Schmidt reaction of alkyl azides and ketones proceeds with retention of configuration of the migrating carbon atom (Eq. 17).[29]



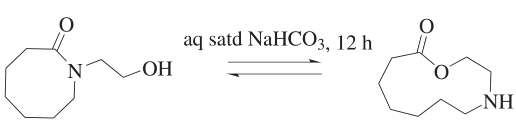
(Eq. 17)

Hydroxyalkyl azides react with aldehydes or ketones under acidic conditions to afford oxocarbenium ions. Once formed, the cation is intercepted by the nucleophilic azido group to afford an azidohydrin-like intermediate that rearranges with loss of nitrogen to afford an iminium ether as the primary product. In the case of aldehydes, where the initial product is a protonated imino ether, loss of both a proton and nitrogen ensue to provide oxazolines or dihydrooxazines when $n = 1$ or 2, respectively (Scheme 6).[45] It is not known whether the proton is lost in concerted elimination reaction or if a 1,2-hydride migration precedes deprotonation.



Scheme 6

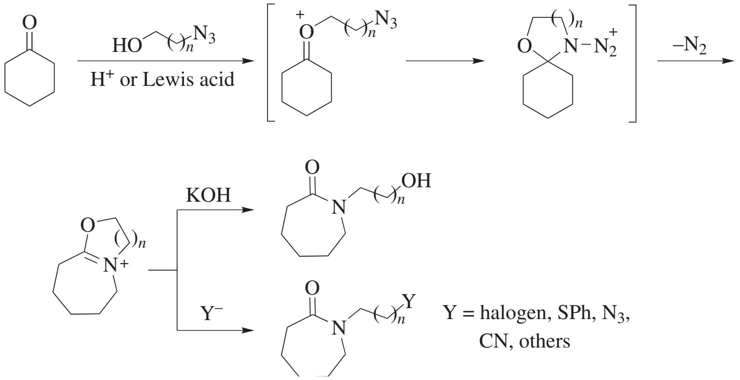
For ketones, the reaction results in an iminium ether as the initial product (Scheme 7). Most often, the iminium ether is converted into an amide by the addition of hydroxide ion. In addition, it may be combined with a variety of other nucleophiles to afford terminally substituted *N*-alkyl lactams.[46] *N*-(Hydroxyalkyl)amides or lactams derived from acyclic or medium-ring ketones are subject to reorganizations to afford amine-substituted esters or lactones, respectively (Eq. 18).[47,48] These reactions are highly structure- and condition-dependent.



I **II**

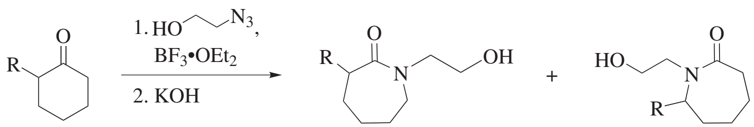
I:**II** = 23:77

(Eq. 18)



Scheme 7

The constitutional outcome of the reactions of unsymmetrical cyclohexanones has been briefly studied (Eq. 19).[49] The extent of migration of the substituted carbon increases with the size of the ketone α-substituent. Interestingly, several ketones bearing an electron-withdrawing group afford a high proportion of the product resulting from migration of the unsubstituted methylene group. These observations have been analyzed by consideration of competing conformational and electronic factors in the azide adducts.[49]

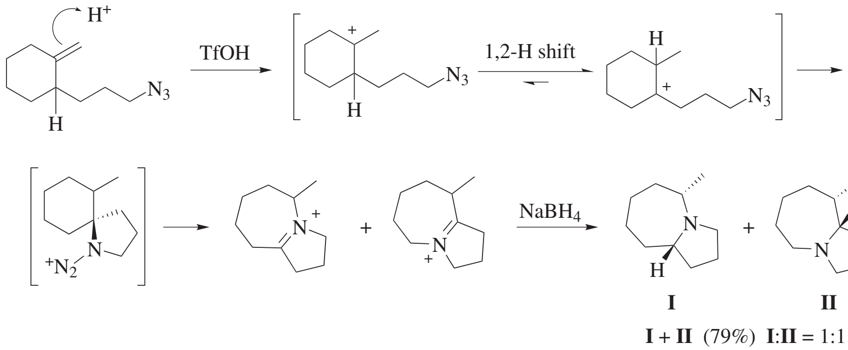


I **II**

(Eq. 19)

R	Yield (%) I + II	I:II
Me	83	45:55
i-Pr	80	21:79
t-Bu	11	13:87
Br	58	>95:5

Alkyl azides also react with carbocations derived from precursors such as alkenes or alcohols. The mechanism of this reaction is analogous to the related reactions of hydrazoic acid, with a key difference being that an intramolecular version is possible for azides. In the reaction shown (Scheme 8),[50,51] the initially generated intermediate is in equilibrium with an isomeric carbocation via a 1,2-hydride migration. Because both are of roughly equal stability, it is likely that the length of the chain between each cation and the azide determines which one will lead to product. In this example, two different carbon-to-nitrogen migration reactions occur to afford a pair of iminium ions as the primary products of the reaction. Because of the small energetic difference between the two possible iminium intermediates in this reaction, a roughly 1:1 mixture of isomers is observed. The addition of an exogenous reducing agent ultimately affords the reduced heterocyclic products via the least sterically hindered direction of hydride attack. The use of other cation precursors will be described in the "Scope and Limitations" section.



Scheme 8

SCOPE AND LIMITATIONS

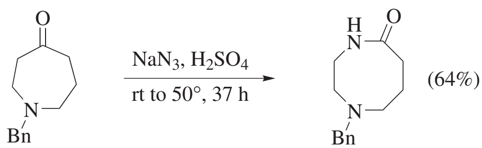
The reaction scope varies greatly with each version of the Schmidt reaction. In general, the reactions of hydrazoic acid with various electrophiles accommodate a broad range of substrates whereas the various Schmidt reactions involving alkyl azides are often more limited.

Schmidt Reactions of Hydrazoic Acid

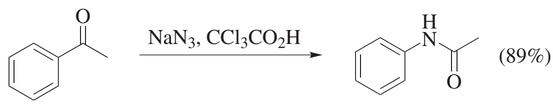
Reactions with Ketones and Aldehydes. The most commonly used Schmidt reaction is the conversion of a ketone into an amide or lactam with hydrazoic acid. The corresponding reactions of aldehydes are less important because they bifurcate into nitriles or insertion products depending on substrates and conditions. Also less useful from a preparative perspective is the use of Schmidt conditions for the conversion of carboxylic acids to provide amines bearing one fewer carbon. In this case, the reaction suffers in comparison with the Curtius rearrangement,[18,52] which carries out the same transformation under milder conditions.

The main practical issues pertinent to ketone/hydrazoic acid reactions are (1) site selectivity, and (2) the formation of tetrazole side products (which can often be minimized by changing the reaction conditions). Many more ketones undergo Schmidt reactions than do not; the most problematic examples are ketones that provide serious steric obstacles to nucleophilic addition to the carbonyl group.

The fact that structurally diverse ketones are so readily available also contributes to the popularity of the Schmidt reaction in synthesis. A noteworthy application is the synthesis of medium-size rings that are hard to make by direct cyclization. Thus, readily available 6- and 7-membered ring ketones are attractive precursors to the corresponding 7- and 8-membered lactams (Eq. 20).[53–56] In contrast, application of the Schmidt reaction to acylic ketones is less common because acyclic amides are effectively made by a passel of coupling methods. The useful application of the Schmidt reaction on an acyclic substrate is the synthesis of aromatic amides from ketone precursors (Eq. 21).[1]

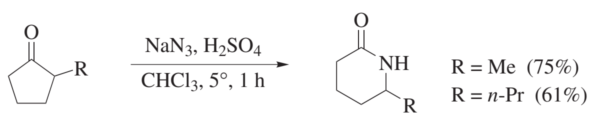


(Eq. 20)

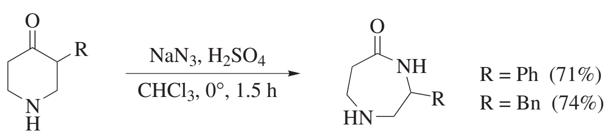


(Eq. 21)

A significant remaining limitation of the Schmidt reaction is that no variant reliably inserts into an α-monosubstituted ketone with migration of the less substituted carbon. For reasons discussed in the previous section, the most substituted α-carbon generally migrates in the reactions of unsymmetrical ketones. Two illustrative examples are shown in Eq. 22[16,53] and Eq. 23.[57]

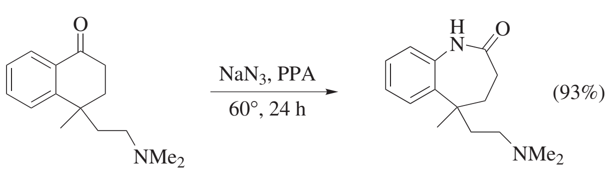


(Eq. 22)

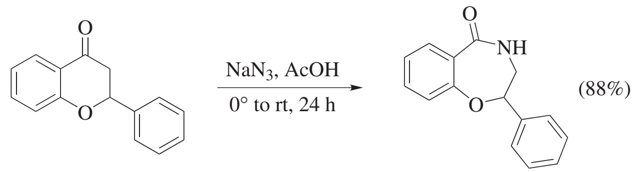


(Eq. 23)

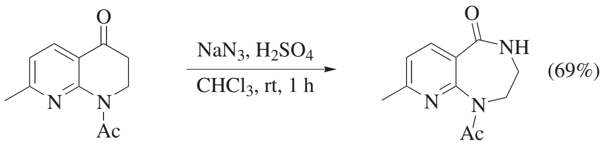
Aromatic ketones often react via migration of the aromatic group (Eq. 24),[58] but exceptions are known. In some cases, these reactions are readily understandable mechanistically; for example, electron-rich aromatic rings should migrate more readily than an alkyl group.[59,60] As discussed in the previous section, the steric demands of the alkyl group also play a role.[7] Other examples are harder to explain; for example, compare Eqs. 24 and 25.[61–64] The migratory preferences in reactions involving heteroaromatic ketones are particularly difficult to predict (Eqs. 26[65] and 27[66]).



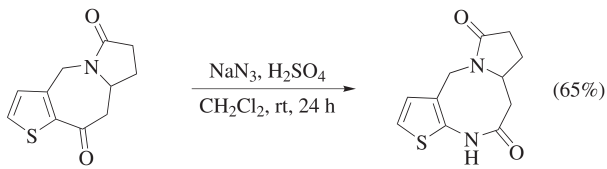
(Eq. 24)



(Eq. 25)

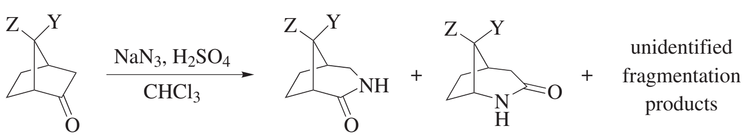


(Eq. 26)



(Eq. 27)

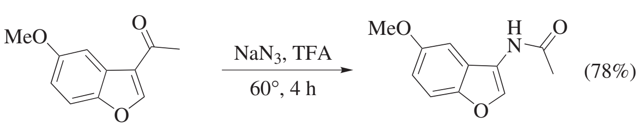
The Schmidt reactions of bicyclic ketones tend to proceed with poor site selectivity and are often accompanied by fragmentation byproducts.[16,67] A few systems, such as norcamphor, react with high selectivity for a particular isomer but the reactions are not necessarily high yielding (Eq. 28).[68]



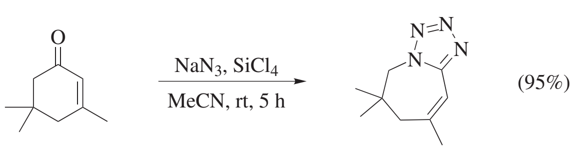
(Eq. 28)

Y = Z = H	(35%)	(<2%)	(63%)
Y = OTs, Z = H	(21%)	(31%)	(48%)
Y = H, Z = OTs	(14%)	(26%)	(60%)

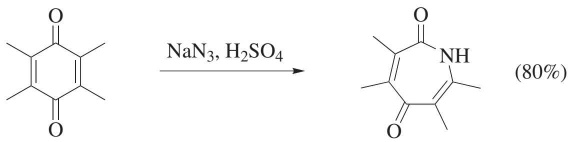
The reaction is also tolerant of α,β-unsaturation with many cases of enones reacting under standard Schmidt conditions. Often a simple enone containing a single adjacent double bond affords a product resulting from migration of the sp^2-hybridized α-carbon (Eq. 29),[69] but exceptions do exist (Eq. 30).[70] Quinones and other compounds containing only adjacent sp^2-hybridized carbons are perfectly competent Schmidt reaction substrates (Eq. 31).[71]



(Eq. 29)

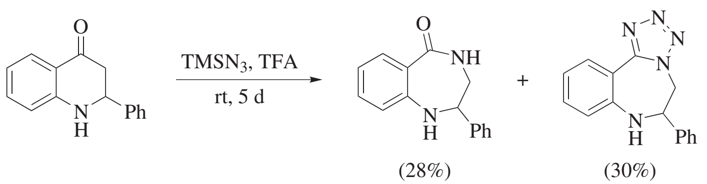


(Eq. 30)

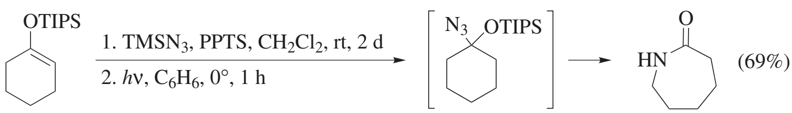


(Eq. 31)

Besides the use of sodium azide and hydrazoic acid in the Schmidt reaction, trimethylsilyl azide provides an alternative source with diminished explosive properties.[72] This reagent reacts with ketones and their enol ethers under acidic conditions (Eq. 32)[73] or irradiation (Eq. 33)[74] to yield lactams. As with the reactions of hydrazoic acid, tetrazoles are often isolated as byproducts in the acid-promoted reactions.

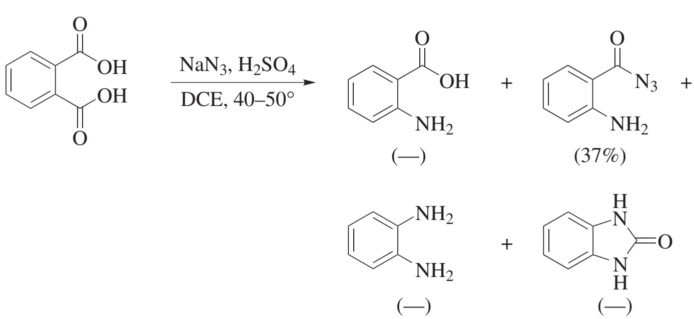


(Eq. 32)



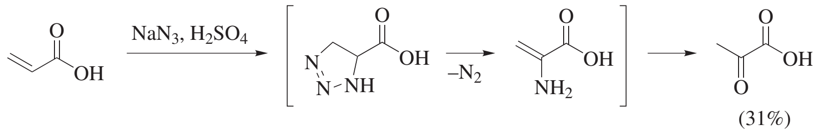
(Eq. 33)

Unusual Reactions and Alternative Electrophiles. A variety of interesting pathways have been reported in the nearly 100 years since the Schmidt reaction was first described.[75–77] This diversity is not surprising given the involvement of high-energy reactive intermediates and does not really detract from the overall utility of the reaction. For example, reaction of phthalic acid affords aniline products from one and two standard Schmidt reactions, respectively, along with a presumed acyl azide intermediate and a urea resulting from intramolecular trapping of an isocyanate (Eq. 34).[78,79] Instead of a Schmidt reaction, acrylic

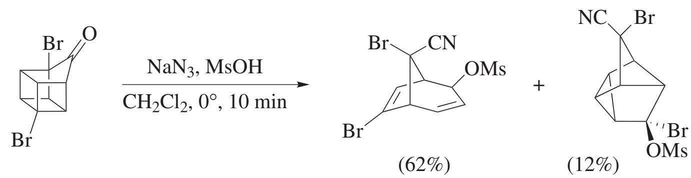


(Eq. 34)

acid undergoes a formal dipolar addition of azide to the double bond followed by acid-promoted decomposition to pyruvic acid (Eq. 35).[80] Similar cycloaddition reactions of alkyl azides are used to effect conversions of α,β-unsaturated ketones into aziridines (see "Schmidt Reactions of Alkyl Azides with Ketones and Aldehydes" section). Highly strained compounds often undergo skeletal rearrangements when exposed to HN_3 (Eq. 36).[81]

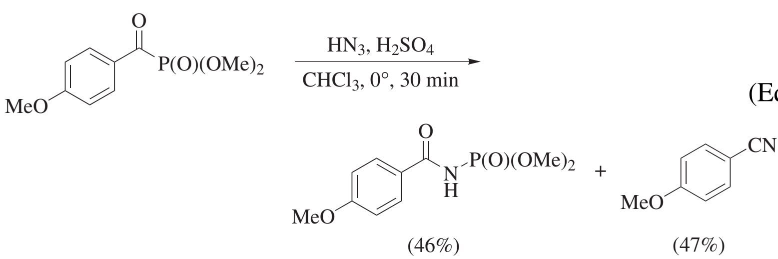


(Eq. 35)

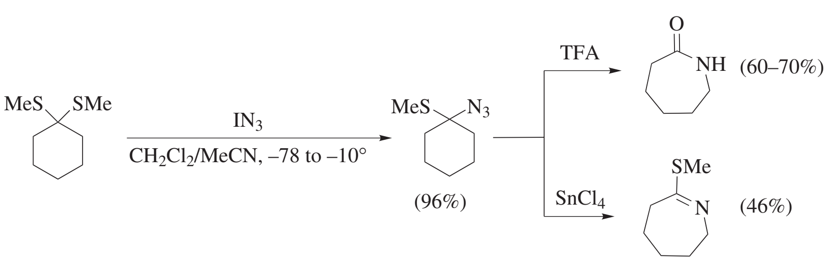


(Eq. 36)

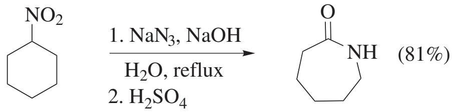
Schmidt reactions also can be carried out with O,O-dialkyl acylphosphonates (Eq. 37).[28,82] In addition, a version of the Schmidt reaction is known in which a dithioketal is activated by treatment with iodine azide to afford an α-azido sulfide (Scheme 9). This intermediate is converted into the corresponding ring-expanded lactam or thioimino ether upon treatment with trifluoroacetic acid or stannic chloride, respectively.[83] Finally, a little-used variation employs nitroalkanes as a carbonyl equivalent. Treatment of nitroalkanes with basic sodium azide affords amides in moderate to good yields (Eq. 38).[84]



(Eq. 37)



Scheme 9

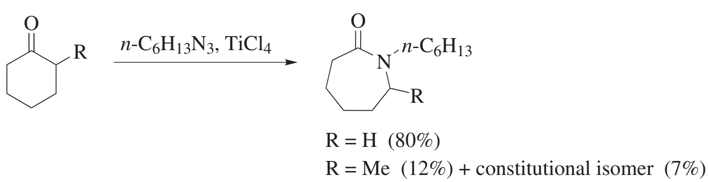


(Eq. 38)

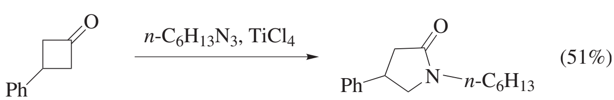
Schmidt Reactions of Alkyl Azides

The reactions of electrophiles with alkyl azides are considerably less general than those with hydrazoic acid. This section is organized according to the electrophile, beginning with a discussion of the reactions of azides with carbonyl groups and their equivalents and moving onto the reactions of alkyl azides with carbocations generated from double bonds or other precursors.

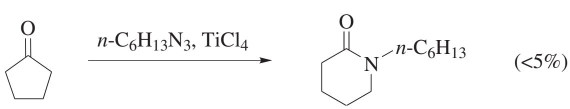
Reactions with Ketones and Aldehydes. The transformation of largest scope in this category involves intramolecular reactions of azidoalkyl-substituted ketones. Intermolecular reactions of azides and ketones have been only sparingly examined to date.[22,85] The known examples of this variation are poorly site selective, often poorly efficient, and limited by even moderate steric hindrance or the size of the ketone ring. The different yields obtained from reactions of *n*-hexyl azide either with cyclohexanone or with 2-methylcyclohexanone (Eq. 39)[22] exemplify the sensitivity of the reaction to additional steric bulk near the reacting carbonyl. Good yields are obtained in a few cases using a strong Lewis acid such as $TiCl_4$.[22,85] Even under these conditions, the reactions are severely limited (Eqs. 40–42). The reaction of alkyl azides with acyclic ketones is of similarly narrow utility.[85]



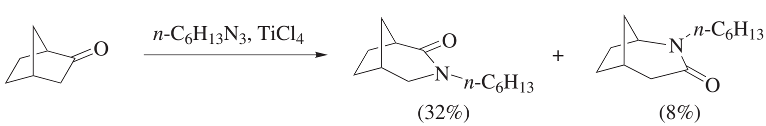
(Eq. 39)



(Eq. 40)

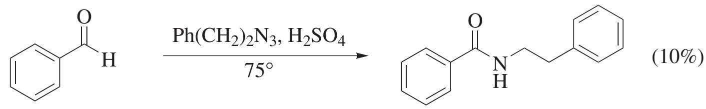


(Eq. 41)



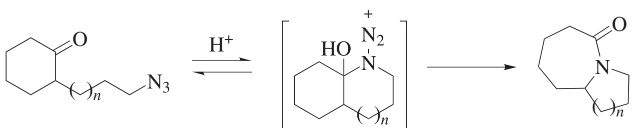
(Eq. 42)

Azides and aldehydes afford amides under protic acid conditions, but only from a few substrates, and in poor yields (Eq. 43).[21]



(Eq. 43)

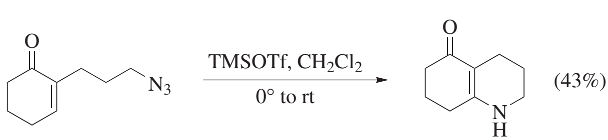
The intramolecular reactions are substantially superior in terms of scope, yields, allowable conditions, and selectivity—nearly every characteristic that one typically associates with synthetic utility. The prime restriction is that the distance between the carbonyl and azide groups must usually be 4 or 5 atoms for high yields. The former is preferred, presumably because it involves the formation of a six-membered cyclic intermediate. Examples involving five carbons typically require stronger Lewis acids (Eq. 44).[3]



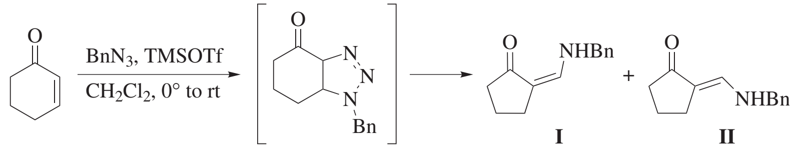
(Eq. 44)

$n = 0$, no reported examples
$n = 1$, TFA, 10 min (93%)
$n = 2$, TFA, 24 h, no conversion
$n = 2$, $TiCl_4$, 16 h (91%)
$n = 3$, no reported examples

The intramolecular process accommodates a great deal of variation in the ketone component such that successful reactions can be achieved with various ring sizes (reactions of cyclic 4–12 membered ketones have been reported[29]) and with acyclic versions. Apart from alkyl substituents, little work has been done to determine which functional groups are tolerated when adjacent to the ketone or the azide group. Electron-withdrawing substituents adjacent to the ketone slow down the reaction but are tolerated.[3] α,β-Unsaturated ketones containing appropriately tethered azides do not provide lactam products but instead afford products of apparent conjugate addition reactions (Eq. 45).[86] In a few cases, lactams have been prepared from α,β-unsaturated ketones upon irradiation (see "Comparison with Other Methods" section). The intermolecular version of this reaction also leads to non-amide products (Eqs. 46[87] and 47[88,89]). Similarly, unsaturated imides react to afford aminohydroxylation products (Eq. 48).[88] Presumably, the Lewis acid activates the enone so that it is more susceptible to 1,3-dipolar cycloaddition rather than 1,2-addition of azide to the ketone.[87]



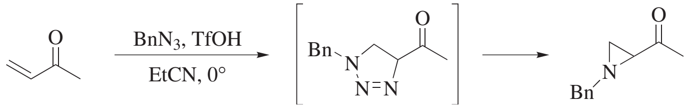
(Eq. 45)



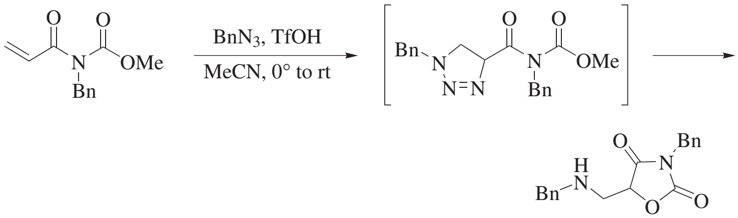
(Eq. 46)

I II

I + **II** (68%) **I**:**II** = 3:2



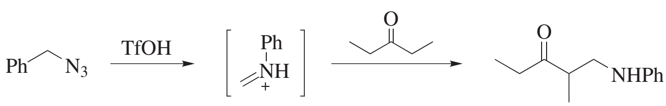
(78%) (Eq. 47)



(Eq. 48)

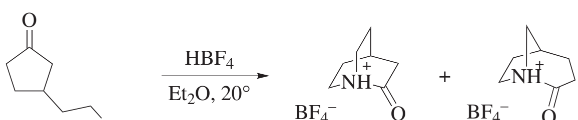
(84%)

Benzylic azides are unreliable partners with saturated ketones in both intermolecular[85] and intramolecular[90] versions of the Schmidt reaction. Thus, in cases where the Schmidt reaction is retarded due to steric crowding or the use of non-optimal tether lengths, the benzylic azides may undergo conversion into iminium ions under the reaction conditions. In such cases, products of Mannich-like processes have been reported (Eq. 49).[85]



(75%) (Eq. 49)

Although possible, reactions affording bridged lactams are rare. One important example entails the reaction of a ketone that bears an azidoalkyl side chain non-adjacent to the carbonyl group, a situation that necessitates bridged lactam formation. One of the two lactams formed is the long-sought "twisted" amide 2-quinuclidone (**1**) (Eq. 50).[91]



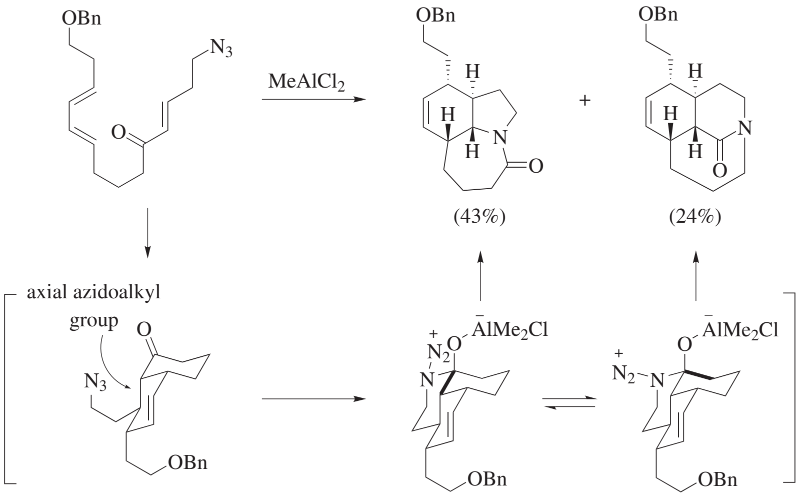
(Eq. 50)

1 **2**

1:**2** = 76:24

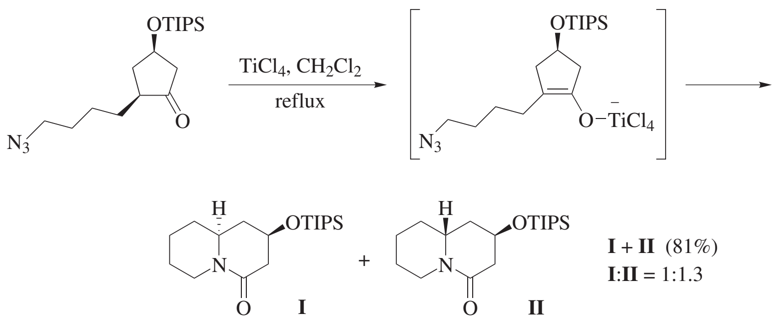
1 (38%) after recrystallization

In another example, intramolecular Schmidt reaction of a complex ketone containing an azidoalkyl group in an axial orientation gives a bridged lactam as a minor product (Scheme 10).[92] The Schmidt substrate is formed by an *endo*-selective intramolecular Diels–Alder reaction (an *exo* Diels–Alder pathway that affords another lactam product in 12% yield is omitted from the scheme). Presumably, two stereoisomeric azidohydrins can form from the intermediate shown, each of which leads to a lactam by antiperiplanar carbon–carbon bond migration with synchronous loss of nitrogen. In this system, one of these intermediates affords the usual fused lactam product whereas the other affords the bridged product.



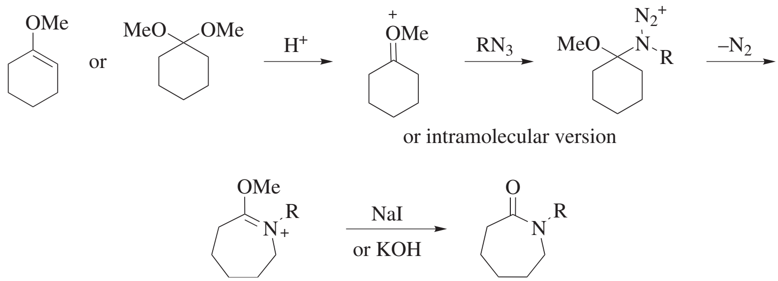
Scheme 10

As noted in the previous section, the intramolecular Schmidt reaction of alkyl azides generally occurs with retention of configuration. However, non-stereoselective reactions are observed in examples in which the carbon α to the carbonyl group undergoes reversible enolization under the reaction conditions (Eq. 51).[93]



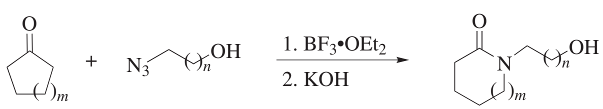
(Eq. 51)

Reactions of Enol Ethers, Ketals, or Hydroxyalkyl Azides. Ketals or enol ethers undergo a closely related reaction with alkyl azides to afford iminium ethers (Scheme 11).[94] In many cases, these intermediates can be isolated and characterized, but are more frequently converted into lactams by treatment of the iminium ether with aqueous base or sodium iodide. The former reaction proceeds via addition of hydroxide to the C=N bond and breakdown of the tetrahedral intermediate, while the latter involves direct S_N2 attack on the *O*-alkyl group. As with the reactions of alkyl azides and carbonyl groups, these reactions are most efficiently carried out intramolecularly.



Scheme 11

In a related process, 1,2- or 1,3-hydroxyalkyl azides react with cyclic ketones to afford lactams after hydrolysis of the primary iminium ether products (Eq. 52).[95,96] These reactions provide practical synthetic equivalents to the direct reactions of alkyl azides with ketones, despite the mechanistic differences (see previous section). This reaction works well for 5- to 7-membered cyclic ketones and is generally tolerant of substitution. Other products resulting from transamidation/transacylation processes may be obtained in reactions of ketones having 7 or more ring atoms (Eq. 18).[47,48]

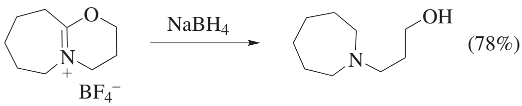


m	*n*	Yield (%)
1	1	96
1	2	98
2	1	98
2	2	90
3	1	68

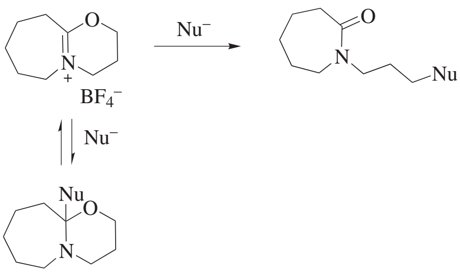
(Eq. 52)

The iminium ether intermediates in these reactions can react with nucleophilic species other than hydroxide. Depending on the nucleophile, reactions at two positions are possible.[46] The site selectivity is rationalized on the basis of reversibility of the initial addition reaction.[97] Thus, kinetic attack occurs at the formal cationic center as exemplified by the irreversible addition of hydride (Eq. 53).[46] However, most nucleophiles react reversibly at this center until they carry out an irreversible S_N2 displacement to afford an ω-functionalized *N*-substituted lactam

(Eq. 54).[46] In the examples shown, the iminium ether intermediate is isolated prior to treatment with the nucleophile (yields are from the iminium ether).



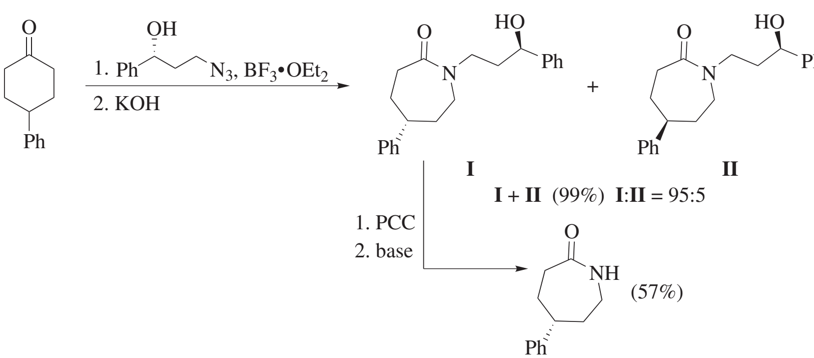
(Eq. 53)



Nu	Yield (%)
PhS	95
PhO	41
F	59
NC	82
N_3	85

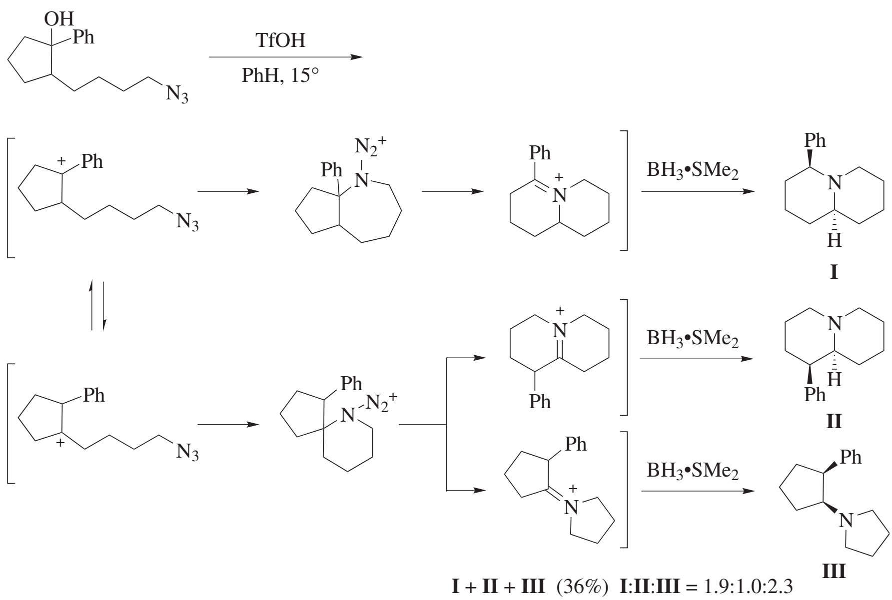
(Eq. 54)

The site selectivity of the Schmidt reaction in 2-substituted cycloalkanones is complex and depends on the substituent (see Eq. 22). However, an interesting mode of selectivity becomes possible in the reactions of symmetrically substituted ketones, such as 4-phenylcyclohexanone, with chiral hydroxyalkyl azides (Scheme 12).[95,98,99] In these cases, the methylene groups adjacent to the ketone are enantiotopic, so that stereoisomeric lactams result depending on which methylene group migrates. These reactions afford up to 95:5 ratios of diastereoisomers in favorable cases. Following separation of the diastereomeric lactams, removal of the nitrogen substituent affords the enantiomerically pure lactam.

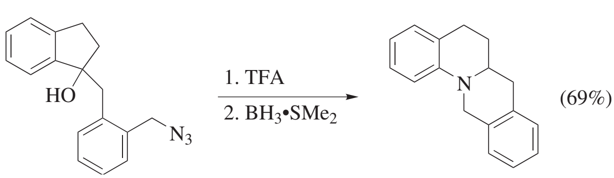


Scheme 12

Reactions with Alkenes, Alcohols, and Other Carbocation Precursors. The reactions of alkyl azides with carbocations, followed by a hydride reduction step, provide amines rather than lactams.[17,23,24,51,100–103] The reaction scope appears to be quite broad for intramolecular reactions. Most of the substrates have four carbons between the azide and the initial site of attack, with examples of both fused and bridged intermediates being reported. In some cases, multiple products are observed due to the intervention of carbocationic rearrangements prior to azide attack (Scheme 13).[101] In addition, each azide adduct is in principle subject to up to six possible alkyl, aryl, or hydride migrations in the ensuing step. In practice, however, only a few of the possible products are generally observed and in many cases careful synthetic planning can steer the reaction toward a single product in high yield (Eq. 55).[102]

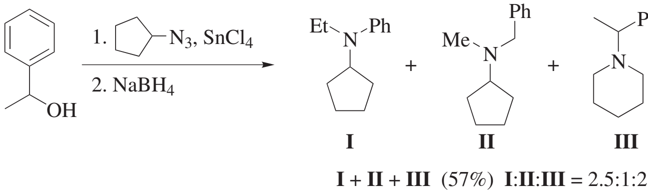


Scheme 13

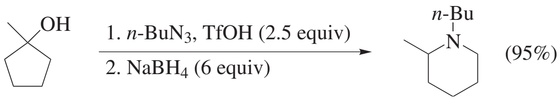


(Eq. 55)

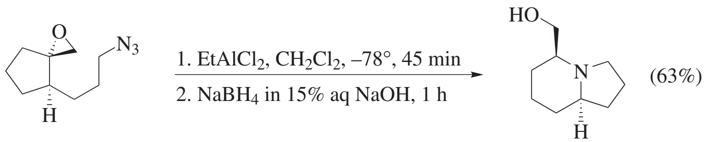
The reactions of benzylic or tertiary carbocations with alkyl azides are also feasible in an intermolecular sense. As in the preceding cases, multiple products resulting from the migration of various groups are often observed (Eq. 56),[17] but in favorable cases the reactions can result in a single product (Eq. 57).[17,24] Epoxides are also effective cation precursors (Eq. 58).[104] As above, the primary product in each of these reactions is an iminium ion that is reduced to afford a tertiary amine.



(Eq. 56)



(Eq. 57)



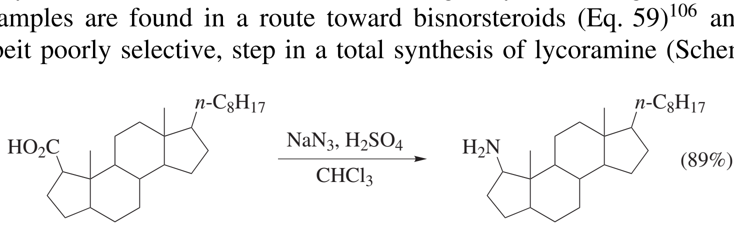
(Eq. 58)

Double bonds are also converted into cation equivalents through the addition of an electrophilic mercury salt (Scheme 14).[50] Attack of azide upon the mercuronium species affords an intermediate that loses nitrogen and undergoes a carbon-to-nitrogen migration. Subsequent addition of reducing agents affords products similar to those obtained when the reaction is promoted by proton sources. In some cases, useful differences in site selectivity are obtained using Hg(II) promotion in comparison to the acid-mediated conversions. Thus, with Hg(II), only products resulting from aryl migration are observed. In contrast, reaction of the same azide under protic conditions affords an approximately equal quantity of products from aryl and alkyl migrations (Scheme 14).[50]

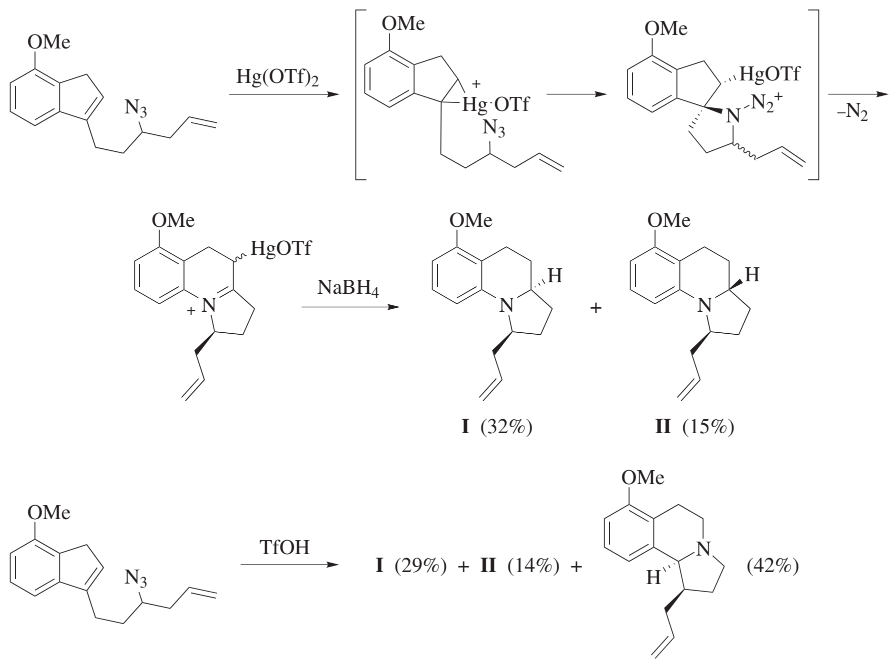
Metal activation of a triple bond provides another electrophilic species that is subject to azide attack (Scheme 15).[105] Thus, treatment of tethered azide-containing alkynes with a gold salt leads to pyrroles via attack of azide. A mechanistic hypothesis involving gold(I)-induced activation of the alkyne toward addition by the proximal nitrogen of the azide is shown. Subsequent loss of dinitrogen produces a cationic intermediate that is stabilized by electron donation from gold. A formal 1,2-shift regenerates the cationic gold(I) catalyst and produces a 2*H*-pyrrole that tautomerizes to the observed product.

APPLICATIONS TO SYNTHESIS

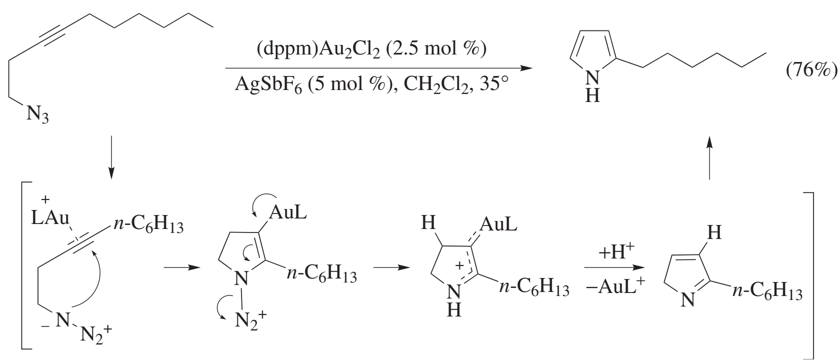
Both inter- and intramolecular Schmidt reactions are encountered as key steps in syntheses of alkaloids and other biologically interesting molecules. Simple examples are found in a route toward bisnorsteroids (Eq. 59)[106] and as a key, albeit poorly selective, step in a total synthesis of lycoramine (Scheme 16).[107]



(Eq. 59)

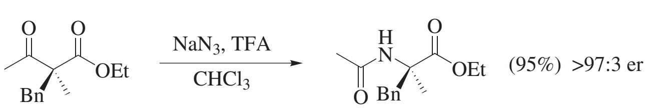


Scheme 14

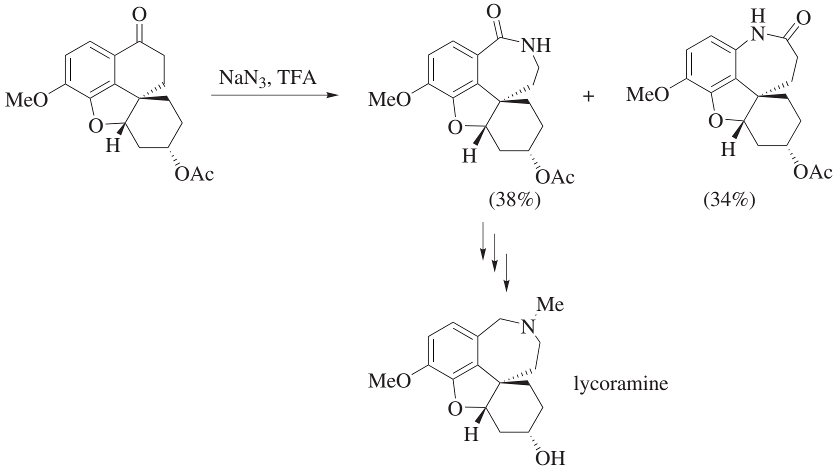


Scheme 15

Several groups have taken advantage of the stereospecificity of the Schmidt reaction en route to non-natural, quaternary amino acid derivatives.[108,109] In this approach, an α,α-disubstituted β-keto ester, prepared by asymmetric alkylation, is subjected to hydrazoic acid to afford the *N*-acetylamino ester with high enantiomeric purity (Eq. 60).[108,109]

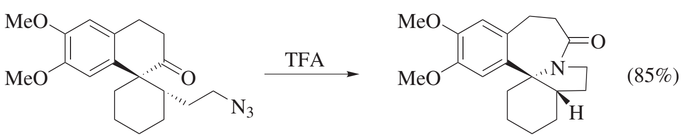


(Eq. 60)



Scheme 16

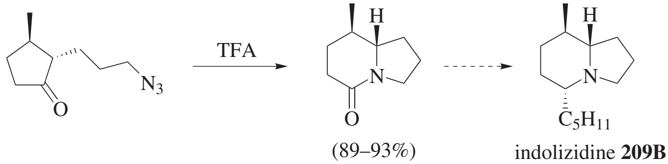
More recent work has used intramolecular Schmidt reactions in routes to multicyclic alkaloid skeletons. An early example was directed toward the homoerythrina spirocyclic ring system (Eq. 61).[110] Instructively, neither Beckmann nor HN_3-mediated Schmidt reaction conditions succeed in converting the corresponding keto mesylate into the lactam. Presumably, the location of the ketone adjacent to a quaternary center limits the facility of intermolecular azidohydrin formation in the latter case.



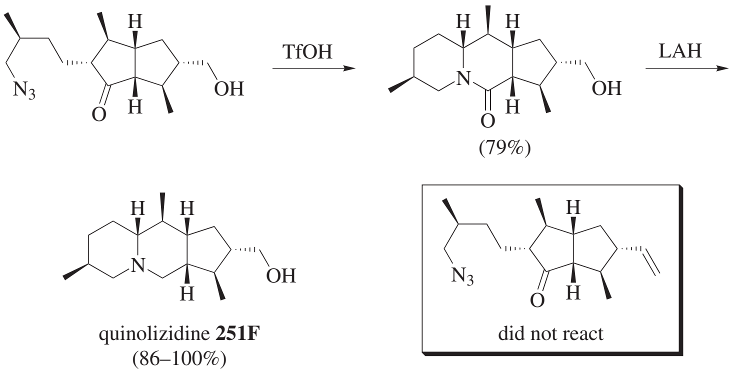
(Eq. 61)

Several applications of the Schmidt reaction have been directed toward alkaloids isolated from South American frogs. The first example, used to synthesize indolizidine **209B**, contains the ideal arrangement of four carbons between the azide and carbonyl groups (Scheme 17).[111] Accordingly, simple dissolution of the azide in trifluoroacetic acid initiates a smooth ring expansion process. On the other hand, the formation of a quinolizidine ring system requires harsher conditions; in the example shown in Scheme 18, triflic acid is needed.[112] Subsequent treatment of the lactam with LAH affords the quinolizidine **251F** (Scheme 18). Notably, the analog with an alkene in place of the terminal alcohol (box) could not be made to react with the azide in this system.

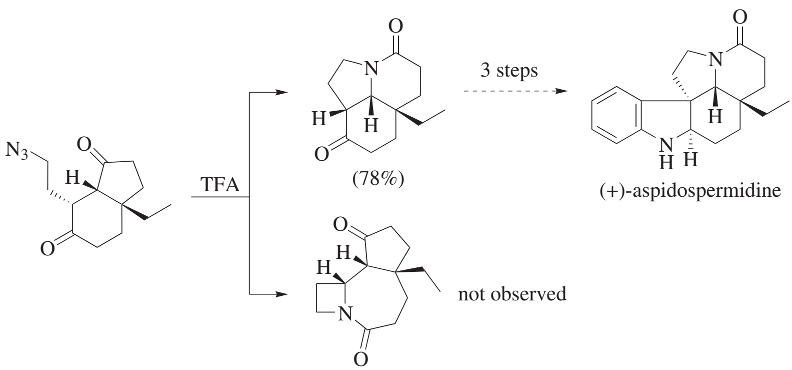
An interesting competition was examined in a route to aspidospermidine (Scheme 19).[113,114] Two lactams can be formed depending on which carbonyl group is attacked by the azide, but only the ketone bearing a 1,6-relationship with the azide reacts. The alternative pathway, which would lead to a product containing a four-membered ring, is not observed.



Scheme 17



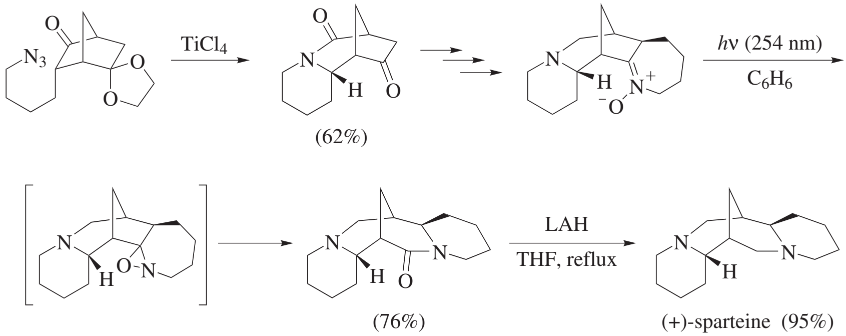
Scheme 18



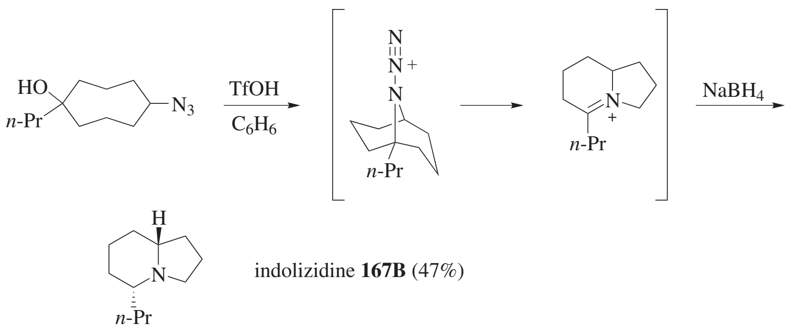
Scheme 19

An intramolecular Schmidt reaction in a bridged ring system is used in the context of a total synthesis of (+)-sparteine (Scheme 20).[115] In this synthesis, the initial Schmidt reaction proceeds smoothly, but it is not possible to use an analogous Schmidt reaction to create the rest of the ring system. A photochemical nitrone rearrangement is ultimately used to complete the synthesis.

An elegant example of a cation-mediated Schmidt reaction is used in a route to another South American frog toxin (Scheme 21).[51,104] In this case, carbocation formation is followed by transannular attack of azide. Only one iminium



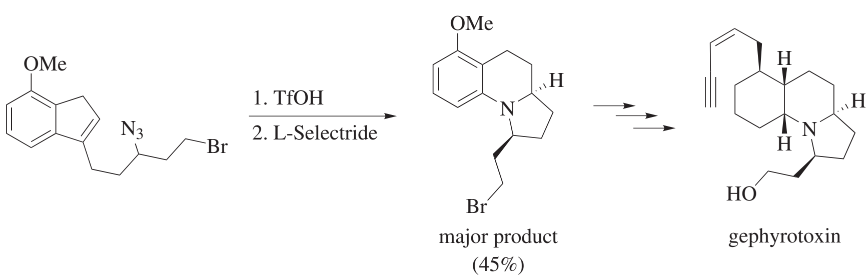
Scheme 20



Scheme 21

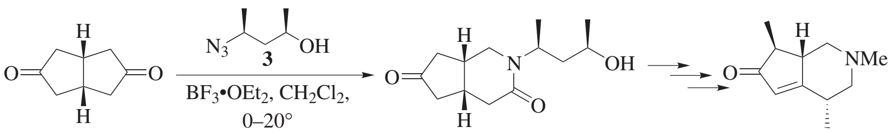
ion can be formed following carbon-to-nitrogen migration because of symmetry. Reduction of this ion occurs stereoselectively to afford indolizidine **167B**.

An additional application of the cation-initiated Schmidt reaction is directed toward a formal synthesis of gephyrotoxin as shown in Scheme 22.[102] The major product involves migration of the phenyl group (a small amount of the alternative alkyl migration product, not shown, is also obtained).



Scheme 22

An asymmetric, hydroxyalkyl-azide-mediated Schmidt reaction is employed in the synthesis of tecomanine.[116] In the key step, the *meso* [3.3.0] bicyclic dione reacts with chiral azide **3** (Scheme 23). Two lactams are formed in a ca. 2:1 ratio; the major isomer **4** is isolated in 40% yield. Removal of the nitrogen substituent and additional modification leads to the natural product.



4 (40%)

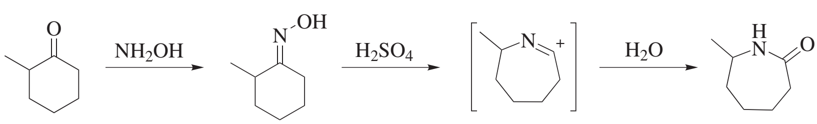
tecomanine

Scheme 23

COMPARISON WITH OTHER METHODS

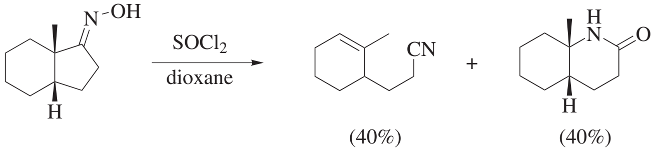
The Schmidt reaction of hydrazoic acid with ketones and the Beckmann reaction are often compared due to the similarity of the electrophiles employed and the products (Scheme 24).[33,117] Unlike the Schmidt reaction, the Beckmann reaction involves two steps: the preparation of an oxime from the starting carbonyl compound followed by either acid treatment or conversion of the hydroxyl group to a leaving group, e.g., by treatment with $POCl_3$. Like the Schmidt reaction using hydrazoic acid, the Beckmann rearrangement is limited to the synthesis of *N*-unsubstituted lactams.

The two reactions are comparable in scope, site selectivity, and synthetic utility. Very often, both Schmidt and Beckmann conditions are investigated when a nitrogen insertion is needed. Although it could be argued that the need for two steps to execute a Beckmann rearrangement is a drawback, in practical terms oxime formation is usually easy and sufficiently high yielding that it does not appreciably detract from using the process. Both sets of procedures have broad scope. Like the Schmidt reaction, the Beckmann rearrangement is also subject to competing nitrile formation from aldehydes. In addition, ketones bearing a cation-stabilizing group in the β position undergo Beckmann fragmentation reactions. Although these reactions have themselves been used to considerable advantage in synthesis, fragmentation when ring expansion is desired is clearly a drawback (Eq. 62).[118,119]



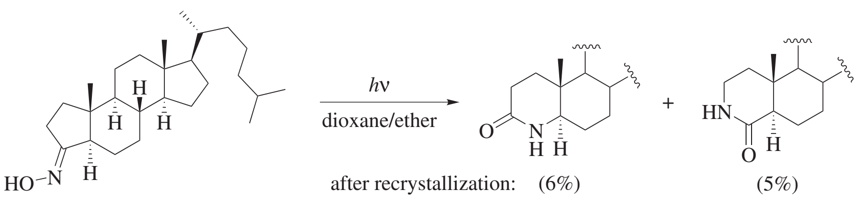
(69%)

Scheme 24

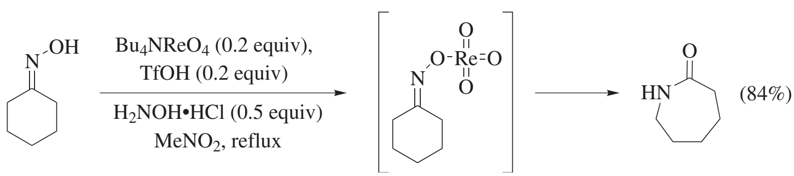


(Eq. 62)

Although exceptions exist, the Schmidt and Beckmann reactions generally afford the same constitutional isomer, i.e., that resulting from migration of the more highly substituted carbon. For the Beckmann reaction, this outcome is due to the preferential formation of the more stable oxime (OH group *anti* to the more bulky group) coupled with stereospecific migration of the antiperiplanar group in the rearrangement step. The similarity of product profiles for a given substrate in the Schmidt and Beckmann reactions has been often used to imply the intermediacy of diazoiminium ethers in the former reaction. Oximes can also be rearranged to provide lactams under photochemical conditions that obviate the need for highly acidic reaction conditions (the photo-Beckmann rearrangement, Eq. 63).[120] Another modification of the Beckmann reaction is promoted by a combination of tetrabutylammonium perruthenate and triflic acid (Eq. 64).[121,122]

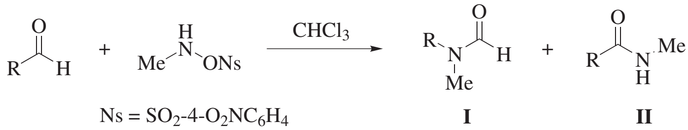


(Eq. 63)



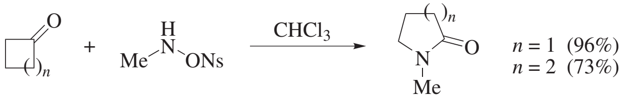
(Eq. 64)

Relatively few alternatives exist to the Schmidt reactions of alkyl azides. One way of directly converting an aldehyde or ketone into an *N*-alkylated amide is to treat the substrate with a reagent of the type $RNHOSO_2Ar$. The initial carbonyl addition step leads to a species that is pre-activated for loss of sulfonate and rearrangement (Eqs. 65[123] and 66[124–127]). Like the intermolecular Schmidt reaction of alkyl azides promoted by $TiCl_4$, this protocol does not have a particularly broad scope but has been usefully employed in particular contexts.



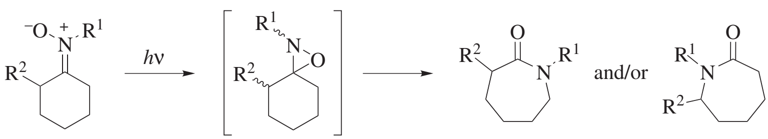
(Eq. 65)

	Yield (%)	
R	I + II	I:II
Ph	96	23:1
4-BrC_6H_4	82	2:1
Et	64	1:7

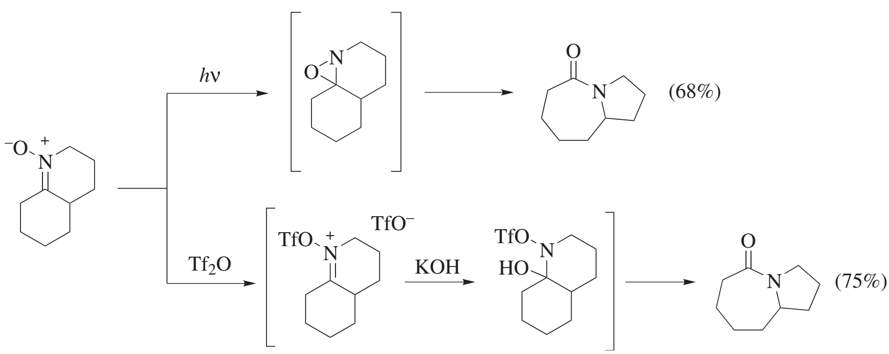


(Eq. 66)

The photochemical rearrangement of nitrones to amides (Eq. 67),[128–131] which also provides *N*-substituted lactams, probably proceeds via the initial rearrangement of the nitrone to the corresponding oxaziridine. This heterocycle then undergoes photochemically mediated in situ rearrangement to the lactam. This reaction has also been explored in the intramolecular context to provide a variety of ring systems.[130,132–136] The reaction can also be promoted by converting the nitrones into their *O*-trifluoromethanesulfonyl derivatives followed by base-mediated rearrangement (Scheme 25).[136] Like the photo-Beckmann reaction, this reaction is useful for cases in which strongly acidic conditions are not desirable.[93,115]



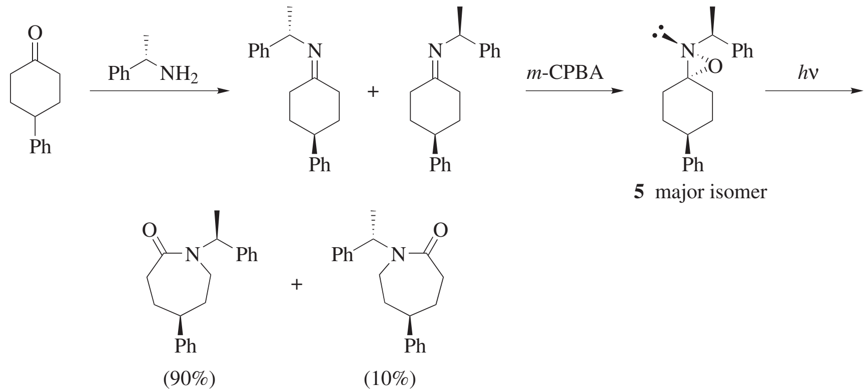
(Eq. 67)



Scheme 25

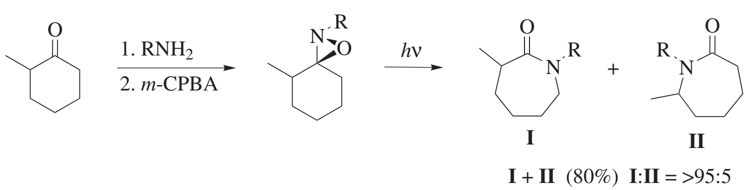
Oxaziridines can also be prepared from ketones or aldehydes via the corresponding imine derivatives, which are oxidized using *m*-CPBA or other common oxidants.[43,137–140] In addition to their likely involvement in photo-Beckmann reactions, oxaziridines are useful precursors to lactams in their own right, via photolytic rearrangement.[78,141–143] Rearrangements can also be induced by treatment with certain low-valent metal salts (iron(II) or copper(I)).[131,144–146]

The photochemical oxaziridine rearrangement is subject to a stereoelectronic effect that has an important synthetic ramification. Chiral oxaziridine **5** (Scheme 26) undergoes stereoselective rearrangement to afford the lactam with 9:1 stereoselectivity. In general, the predominant product from such photochemical rearrangements results from migration of the bond antiperiplanar to the lone pair on the oxaziridine nitrogen atom (which is non-invertable under the reaction conditions).[147,148]



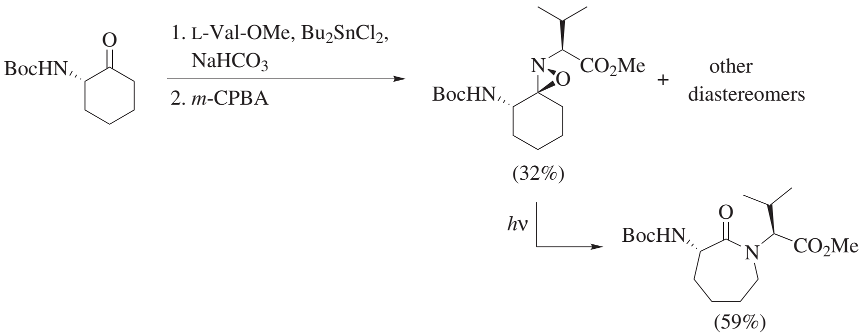
Scheme 26

Because of this effect, the oxaziridine rearrangement reaction is the only nitrogen insertion reaction known that provides a reliable route to lactams resulting from migration of the less substituted carbon in unsymmetrical cycloalkanones (Scheme 27).[149–151] Thus, the oxaziridine intermediate that is generally formed places the N-alkyl group away from the more highly substituted carbon on the ketone.[142] An example using this strategy to prepare a series of peptide analogs is shown in Scheme 28.[152]



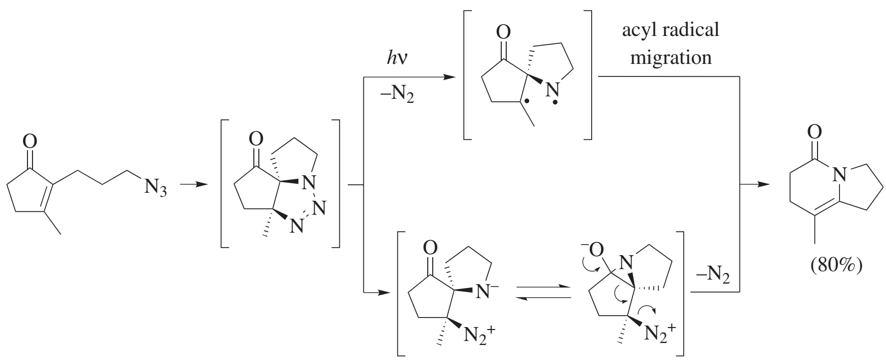
Scheme 27

A significant limitation of the intramolecular Schmidt reaction of alkyl azides is its inapplicability to unsaturated ketones (Eq. 45). In contrast, insertion products



Scheme 28

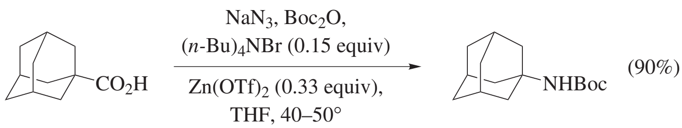
of azides appended to such partners are observed under irradiation.[153–156] These reactions are proposed to involve a thermally allowed [3+2] cycloaddition onto the enone, photochemical generation of a diradical with loss of dinitrogen, and finally molecular reorganization to afford the final products (Scheme 29).[86] An ionic mechanism may also be operative in this case.



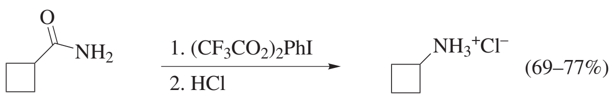
Scheme 29

As noted earlier, the Schmidt reactions of hydrazoic acid with carboxylic acids or with aldehydes are rarely used by synthetic chemists. In the former case, the Curtius reaction of carboxylic acids, which involves the conversion of the carboxylic acid into an acyl azide that is then subjected to thermal rearrangement, is the most common reaction for the synthesis of amines from acids. The acyl azide can be prepared via the acyl chloride (typically readily made from the acid), other kinds of activated acids,[157] or directly from the acid via in situ activation, e.g., by reaction with diphenyl phosphoryl azide.[158]

The Curtius reaction has been widely adopted because its conditions are relatively mild and do not require the use of the toxic and explosive hydrazoic acid as a reagent. In addition, the thermal acyl azide rearrangement provides as its initial product an isocyanate; hydrolysis of this species with water affords the amine. Even better, the isocyanate can be combined with alcohols or amines to afford carbamates or ureas, respectively. A one-pot version of the Curtius reaction that provides N-Boc amines in 50–94% yields has also been reported (Eq. 68).[159] Another widely used reaction that does not involve the formation of N_3-containing species is the Hofman rearrangement of amides to afford amines (Eq. 69).[160]



(Eq. 68)



(Eq. 69)

EXPERIMENTAL CONDITIONS

Schmidt reactions using hydrazoic acid are generally accomplished by generating HN_3 in situ from NaN_3, i.e., by adding it to sulfuric acid, HCl, or polyphosphoric acid.[161] Cosolvents such as chloroform or DME may be used. In some cases, an additional protic or Lewis acid such as $SnCl_4$, trichloroacetic acid, or $BF_3{\bullet}OEt_2$ is added. Heating is often required. Some older procedures involve preparation of stock solutions of HN_3 in chloroform or other solvents, although these are rarely used nowadays.[11]

The use of hydrazoic acid is hazardous, as it is both explosive and toxic. Proper precautions that include safety shields and an efficient hood are essential. Typically, the workup of the reaction involves a basic extraction step that makes it possible to remove hydrazoic acid in the aqueous layer (as NaN_3 for example). For reasons discussed below, it is best not to use methylene chloride as the organic solvent in such extractions.

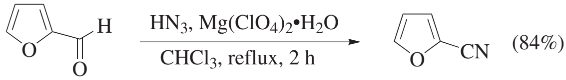
Intermolecular Schmidt reactions in which alkyl azides react with carbonyl compounds are generally carried out in methylene chloride using commercial solutions of $TiCl_4$. Intramolecular reactions can be carried out under similar conditions, although a wider range of Lewis acids are usable for these more reactive substrates. Alternatively, protic acid conditions can be used, with neat trifluoroacetic acid or triflic acid/methylene chloride being most common in this context. Similar conditions can be employed for the reactions of azides with cations derived from olefins or alcohols.

Either protic or Lewis acids can be used to facilitate the intermolecular reactions of hydroxyalkyl azides with ketones; a comparative study suggests that $BF_3{\bullet}OEt_2$ is the most effective promoter for this reaction.[96] The key difference between these reactions and those noted above is that the initial product is not a lactam or amide but rather an iminium ether. These salts can be isolated using standard workup conditions and in some cases have been chromatographed. Treatment with an aqueous base like KOH or $NaHCO_3$ is commonly used to convert these initial products into lactams.

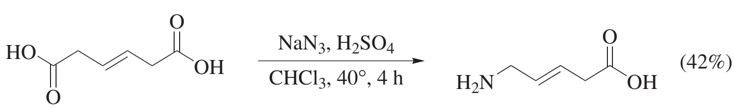
Two safety considerations come into play for the reactions with alkyl azides. The first is the nature of the azide itself. *The authors advise readers to assume that any alkyl azide is a possible explosion hazard and to treat azides having low formula weights with particular caution.* Specific manipulations to be avoided include heating (especially in the absence of solvent), vacuum distillation, preparing on large scale, or allowing exposure to metals.

A second consideration should be heeded when preparing azides from sodium azide. *NaN_3 is believed to pose a particular hazard when heated or evaporated in methylene chloride solutions; the formation of diazidomethane is possible under these conditions and explosions have been documented.*[162] One can also prepare alkyl azides via halogen displacement or epoxide opening by azidotrimethylsilane activated by fluoride or a Lewis acid.[163,164] However, *azidotrimethylsilane has been associated with toxic reactions, possibly by environmental hydrolysis to form hydrazoic acid.*[165] Finally, a variation of the Mitsunobu reaction using $Zn(N_3)_2$ can be used to prepare azides directly from alcohols.[166]

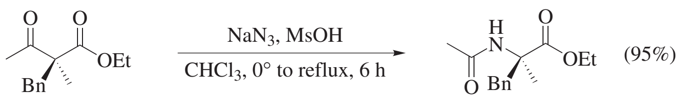
EXPERIMENTAL PROCEDURES



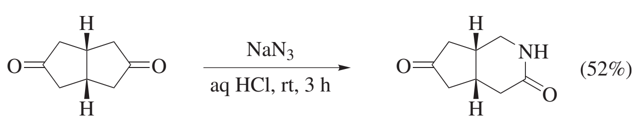
Furan-2-carbonitrile [Schmidt Reaction of an Aldehyde with Hydrazoic Acid to Afford a Nitrile].[167] To a three-necked flask with a mechanical stirrer and a reflux condenser were added 2-furaldehyde (9.61 g, 0.1 mol), a solution of HN_3 in $CHCl_3$ (15 mL, 0.11 mol), and $Mg(ClO_4)_2$ (25.0 g, 0.1 mol). The release of gaseous nitrogen began after 5 min. The flow of nitrogen became strongest after 10 to 15 min. When the release of nitrogen had stopped, the reaction mixture was brought to its boiling point and kept there for 2 h. The contents of the flask were cooled to rt, water was added, and the mixture was filtered. The organic layer was washed twice with water, dried (Na_2SO_4), and evaporated. The residue was distilled under vacuum to give the desired product (7.82 g, 84%): bp 147°; ^1H NMR (300 MHz, $CDCl_3$) δ 6.63 (dd, J = 1.8, 3.7 Hz, 1H), 7.33 (d, J = 3.7 Hz, 1H), 7.82 (d, J = 0.75 Hz, 1H); IR (neat) 3110, 2200, 1575 cm^{-1}. Anal. Calcd for C_5H_3NO: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.44; H, 3.61; N, 14.91.



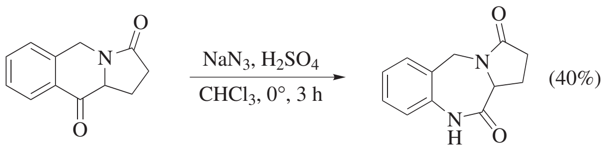
(*E*)-5-Aminopent-3-enoic Acid [Schmidt Reaction of a Carboxylic Acid with Hydrazoic Acid to Afford an Amine].[168] (*E*)-2-Butene-1,4-dicarboxylic acid (1.4 g, 9.71 mmol) was suspended in $CHCl_3$ (40 mL), and concentrated sulfuric acid (4.0 mL) was added. NaN_3 (0.65 g, 10 mmol) was added in small amounts over 30 min while the mixture was stirred rapidly. After a further 4 h at 40° the $CHCl_3$ layer was decanted from the viscous residue which was washed again with $CHCl_3$ (30 mL). The residue was dissolved in water (150 mL), filtered, and added to a column of Dowex 50 W (H^+) ion-exchange resin (50 mL). The column was washed with water to neutral pH and then the amino acid was eluted with aqueous pyridine (300 mL, 1 M). Evaporation of the solvent afforded an oil (600 mg) that slowly solidified. Recrystallization from water/ethanol gave the desired product as white needles (0.437 g, 42%): mp 165–167°; IR (nujol) 3500–2400, 2180, 1625 cm^{-1}; ^{1}H NMR (89.6 MHz, D_2O/DCl) δ 3.64 (d, J = 6.1 Hz, 2H), 4.03 (d, J = 5.7 Hz, 2H), 6.28 (m, 2H); MS (EI) m/z: $[M + H]^+$ 116 (100), 99 (86), 98 (11), 85 (10), 70 (13). Anal. Calcd for $C_5H_9NO_2$: C, 52.2; H, 7.9; N, 12.2. Found: C, 52.0, H, 7.9; N, 12.4.



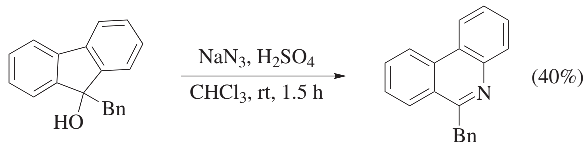
(*R*)-Ethyl 2-Acetamido-2-methyl-3-phenylpropanoate [Schmidt Reaction of an Acyclic Ketone with Hydrazoic Acid to Afford an Amide].[109] Methanesulfonic acid (0.73 mL, 10.0 mmol) was added dropwise to the stirred solution of ethyl (*S*)-2-benzyl-2-methylacetoacetate (234 mg, 1.00 mmol) in $CHCl_3$ (5 mL) at 0°, and then NaN_3 (325 mg, 5.0 mmol) was added. After being refluxed for 6 h, the reaction mixture was cooled to rt, diluted with H_2O, neutralized with diluted aqueous NH_3, extracted with Et_2O, and dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (hexane/EtOAc 9:1) to give the desired product as a colorless oil (237 mg, 95%): $[\alpha]^{25}{}_D - 63.8$ (c 1.10, $CHCl_3$), lit. $[\alpha]_D - 47.8$ (>97.5:2.5 er); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 3.0 Hz, 3H), 1.66 (s, 3H), 1.96 (s, 3H), 3.21 (d, J = 13.5 Hz, 1H), 3.60 (d, J = 13.5 Hz, 1H), 4.29 (m, 2H), 6.09 (br s, 1H), 7.02–7.08 (m, 2H), 7.18–7.30 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.1, 23.4, 24.0, 41.0, 61.2, 61.8, 126.8, 128.2, 129.8, 136.6, 169.5, 173.9; IR (neat) 3300 (br), 1720, 1660 cm^{-1}. FABMS m/z: $[M + H]^+$ 250.



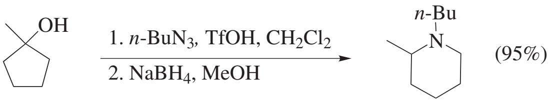
(1*R, 6*S**)-3-Azabicyclo[4.3.0]nona-4,8-dione [Schmidt Reaction of a Cyclic Ketone with Hydrazoic Acid to Afford a Lactam].[116]** Sodium azide (0.60 g, 9.1 mmol) was added portionwise over 20 min to a solution of *cis*-bicyclo[3.3.0]octane-3,7-dione (1.0 g, 7.2 mmol) in 36% aqueous HCl (20 mL), while keeping the temperature below 35°. The mixture was stirred for 3 h at rt and then brought to pH 10 with 20% aqueous NaOH at 0°. Precipitated NaCl was filtered off and the aqueous layer was extracted continuously with $CHCl_3$ for 48 h. Drying the organic phase over $MgSO_4$, followed by removal of solvent, furnished a residue that was separated on a silica gel column (30 g). Elution with CH_2Cl_2/acetone (85:15) gave unreacted diketone (240 mg) and the desired product (576 mg, 52%): mp 120–122°; ^1H NMR ($CDCl_3$) δ 2.10–2.30 (m, 3H), 2.40–2.90 (m, 5H), 3.21 (ddd, J = 3.0, 6.8, 13.0 Hz, 1H), 3.52 (ddd, J = 3.5, 5.8, 13.0 Hz, 1H), 6.3 (br s, 1H); ^{13}C NMR (D_2O) δ 30.7 (d), 31.3 (d), 31.9 (t), 40.9 (t), 41.9 (t), 43.6 (t), 175.4 (s), 223.7 (s); IR (neat) 3246, 2935, 1735, 1667, 1638 cm^{-1}; MS m/z: M^+153 (100), 125 (10), 112 (33), 96 (35), 82 (53), 68 (33), 54, (82), 41 (78). Anal. Calcd for $C_8H_{11}NO_2$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.76; H, 7.21; N, 9.11.



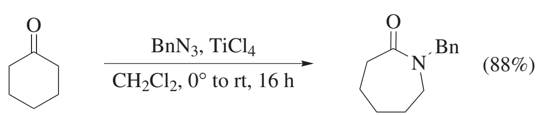
10,11a-Dihydro-1*H*-benzo[*e*]pyrrolo[1,2-*a*][1,4]diazepine-3,11(2*H*,5*H*)-dione [Schmidt Reaction of a Heterocyclic Ketone with Hydrazoic Acid to Afford a Lactam].[169] To a solution of 1,2-dihydropyrrolo[1,2-*b*]isoquinoline-3,10(5*H*,10a*H*)-dione (1.5 mmol) in $CHCl_3$ (30 mL) at 0°, was added concentrated sulfuric acid (24.3 mL). NaN_3 (214 mg, 3.3 mmol) was added portionwise and the mixture was stirred for 3 h at this temperature. Ice (250 g) was then added. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the organic extracts were washed with water (2 × 25 mL) and dried over $MgSO_4$. After evaporation under vacuum, the crude product was purified by chromatography on a silica gel column (240–400 mesh) using CH_2Cl_2/MeOH (99:1, v/v) as eluent to give the desired product (40%): mp 202–204°; ^1H NMR ($CDCl_3$) δ 2.00–2.10 (m, 2H), 2.40–2.70 (m, 2H), 4.18 (q, J = 7.1 Hz, 1H), 4.28 (d, J = 14 Hz, 1H), 4.77 (d, J = 14 Hz, 1H), 7.09 (d, J = 8 Hz, 1H), 7.22 (d, J = 8 Hz, 1H), 7.35 (d, J = 8 Hz, 1H), 7.37 (d, J = 8 Hz, 1H), 8.06 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.75, 29.9, 44.6, 57.8, 122.1, 126.4, 127.3, 129.6, 130.4, 136.8, 169.3, 173.4; IR (neat) 3160, 1670 cm^{-1}; MS m/z: M^+ 216. Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.95. Found: C, 66.39; H, 5.47; N, 13.18.



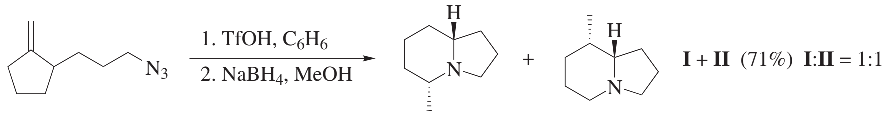
9-Benzylphenanthridine [Schmidt Reaction of an Alcohol and Hydrazoic Acid to Afford an Imine].[170] To a suspension of NaN_3 (7.3 g, 11.0 mmol) in $CHCl_3$ (15 mL), cooled in ice, was added dropwise sulfuric acid (98%, 29 mL) with stirring that was continued for 10 min at 0°. The ice bath was replaced by a water bath maintained at rt, and a solution of 9-benzylfluoren-9-ol (2.0 g, 7.3 mmol) in $CHCl_3$ (20 mL) was added during 1 h to the vigorously stirred mixture. Stirring was continued for a further hour; the mixture was then poured on ice (1.2 kg) and shaken. From the aqueous acidic solution, and from the sulfate (which frequently separated), the base was liberated by addition of 2 N NaOH. The product was filtered off, washed, and dried. The desired product was obtained after crystallization from ethanol and short-path distillation at 130°/0.4 mm as yellow needles (0.8 g, 40%): mp 112°. Anal. Calcd for $C_{20}H_{15}N$: C, 89.2; H, 5.6; N, 5.2. Found: C, 88.7; H, 5.7; N, 5.15.



1-(*n*-Butyl)-2-methylpiperidine [Schmidt Reaction of an Alcohol with an Alkyl Azide to Afford an Amine].[24] Triflic acid (0.959 g, 6.33 mmol) was added to a solution of 1-methylcyclopentan-1-ol (0.250 g, 2.49 mmol) and *n*-butyl azide (1.48 g, 15.0 mmol) in CH_2Cl_2 at 0° over 10 min. Sodium borohydride (1.25 g, 38.0 mmol) in MeOH (10 mL) was added at 0°. After stirring at rt overnight, 2 N HCl (10 mL) was added and the mixture was washed with ether (2 × 20 mL), then basified with aqueous 15% NaOH (30 mL) and extracted with ether (2 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4, and concentrated to afford the desired product as a clear oil (0.369 g, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3H), 1.06 (d, J = 6.3 Hz, 3H), 1.20–1.33 (m, 4H), 1.35–1.50 (m, 2H), 1.52–1.68 (m, 4H), 2.12 (dt, J = 3.0, 10.6 Hz, 1H), 2.21–2.30 (m, 1H), 2.31–2.38 (m, 1H), 2.58–2.72 (m, 1H), 2.80–2.90 (m, 1H); ^{13}C NMR (90 MHz, $CDCl_3$, JMOD) δ 14.0, 19.1, 20.9, 24.1, 26.2, 27.2, 34.6, 52.1, 53.8, 55.70; IR (neat) 2859 (s), 2786 (s), 2592 (w), 1455 (m), 1372 (m), 1330 (w), 1277 (w), 1132 (w), 1076 (w), 900 (w) cm^{-1}; MS (EI) m/z: M^+ 155 (12.6), 140 (59.4), 126 (5.3), 112 (100), 98 (9.7), 84 (20.1), 70 (6.1), 55 (18.1), 44 (18.5). HRMS m/z: calcd for $C_{10}H_{21}N$, 155.1674; found, 155.1669.

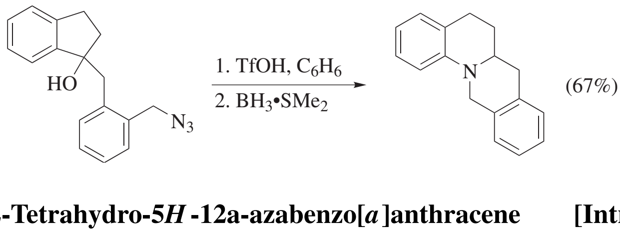


1-Benzyl-2*H*-hexahydroazepin-2-one [Intermolecular Schmidt Reaction of a Ketone with an Alkyl Azide to Afford an Amide].[85] To a solution of cyclohexanone (0.100 g, 1.02 mmol) and benzyl azide (0.271 g, 2.04 mmol) in CH_2Cl_2 (2.5 mL), in an ice bath, was added dropwise $TiCl_4$ (0.484 g, 2.55 mmol). The reaction mixture was allowed to warm to rt (with gas evolution). A precipitate formed after 15 min, and the suspension was stirred for a total of 16 h, at which time it was diluted with EtOAc (20 mL) and partitioned between EtOAc (200 mL) and saturated $NaHCO_3$ solution (30 mL). The organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by silica gel chromatography (hexanes/EtOAc 4:1) gave the desired product as a clear oil (0.365 g, 88%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.46–1.53 (m, 2H), 1.70–1.75 (m, 4H), 2.64–2.66 (m, 2H), 3.26–3.33 (m, 2H), 4.60 (s, 2H), 7.26–7.32 (m, 5H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 23.4, 28.0, 29.9, 37.1, 48.8, 51.0, 127.2, 128.1, 128.4, 137.8, 175.9; IR (neat) 2923, 1637 cm^{-1}; MS (EI) m/z: M^+ 203, 106, 91, 55. HRMS m/z: calcd for $C_{13}H_{17}NO$, 203.1310; found, 203.1313.

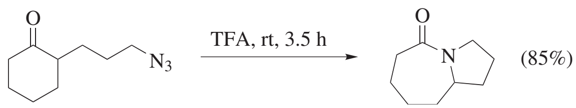


I II

(5*R,8a*R**)-5-Methylindolizidine and (8*S**,8a*S**)-8-Methylindolizidine [Intramolecular Schmidt Reaction of an Azidoalkyl Alkene to Afford an Amine].[51]** Triflic acid (1.250 g, 8.34 mmol) was added to a cooled (5°) solution of 1-(3-azidopropyl)-2-methylenecyclopentane (0.920 g, 5.56 mmol) in benzene (55 mL). After 45 min, $NaBH_4$ (0.631 g, 16.7 mmol) was added via a pressure equalizing solid addition funnel. Methanol (10 mL) was immediately added, and the resulting mixture was stirred for 10 h. Aqueous NaOH (25 mL, 15% w/v) was added, and the resulting mixture was extracted with ether (3 × 15 mL). The combined organic extracts were washed with brine (2 × 25 mL) and water (2 × 25 mL), then dried ($MgSO_4$) and concentrated. Silica gel was deactivated by the addition of 20% by weight of hexamethyldisilazane to a suspension of SiO_2 in hexane. Chromatography on the deactivated silica gel (hexane/acetone 88:12) afforded a 1:1 mixture of the title compounds (0.546 g, 71%) as an inseparable mixture as determined by GC analysis: ^{1}H NMR (on mixture, 360 MHz, $CDCl_3$) δ 0.84 (s, 1H), 0.86 (s, 1H), 0.95 (dd, 1H), 1.07 (s, 1H), 1.09 (s, 1H), 1.1–2.1 (m, 18H), 2.95–3.1 (m, 2H), 3.15–3.25 (m, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 18.9, 20.5, 21.1, 23.3, 24.7, 25.8, 29.1, 30.6, 31.1, 33.5, 34.3, 36.9, 51.8, 52.9, 54.6, 58.9, 64.8, 70.9; IR (on mixture, neat) 2928 (s), 2779 (s), 2370 (m), 2274 (m), 1457 (m), 1328 cm^{-1}. Data for (5*R**,8a*R**)-5-methylindolizidine: MS (EI) m/z: M^+ 139, 138, 124 (100), 110, 97, 96, 70, 69, 68, 57, 56, 55, 54, 42, 41, 39. GCMS data for (8*S**,8a*S**)-8-methylindolizidine: MS (EI) m/z: M^+ 139, 138, 124, 111, 110, 97, 96 (100), 84, 83, 82, 70, 69, 68, 67, 56, 55, 54, 53, 43, 42, 41, 40, 39.



6,6a,7,12-Tetrahydro-5*H*-12a-azabenzo[*a*]anthracene [Intramolecular Schmidt Reaction of an Azidoalkyl Alcohol to Afford an Amine].[102] Triflic acid (0.339 g, 2.26 mmol) was added to a solution of 1-[2′-(azidomethyl)benzyl]-2,3-dihydro-1*H*-inden-1-ol (0.544 g, 1.95 mmol) in benzene (30 mL) at rt. After 10 min, the solution was cooled to 0° and treated with borane dimethyl sulfide complex (3.0 mL of a 2.0 M solution in THF, 6.0 mmol). After the mixture was warmed to rt with stirring for 14 h, 15% aqueous NaOH (15 mL) was added, and the resulting mixture was extracted with ether (3 × 15 mL). The combined organic extracts were washed with brine, then dried ($MgSO_4$) and concentrated. Chromatography (hexane/ether 7:1) afforded the desired compound (0.307 g, 67%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.87–1.96 (m, 1H), 2.01–2.11 (m, 1H), 2.65–2.96 (m, 4H), 3.30–3.38 (m, 1H), 4.22 (d, J = 15.8 Hz, 1H), 4.76 (d, J = 15.8 Hz, 1H), 6.66–6.71 (m, 1H), 6.83 (d, J = 8.2 Hz, 1H), 7.00 (d, J = 7.3 Hz, 1H), 7.12–7.21 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.7, 29.7, 37.5, 50.3, 53.1, 112.1, 117.2, 125.2, 126.0, 126.1, 126.3, 127.1, 128.2, 128.3, 134.2, 134.8, 146.1; IR (neat) 1603 cm^{-1}; MS (EI) m/z: M$^+$ 235 (100), 220, 84; HRMS m/z: calcd for $C_{17}H_7N$, 235.1361; found, 235.1352.



Hexahydro-1*H*-pyrrolo[1,2-*a*]azepin-5(6*H*)-one [Intramolecular Schmidt Reaction of an Azidoalkyl Ketone to Afford a Lactam].[29] 2-(3-Azidopropyl) cyclohexanone (0.099 g, 0.55 mmol) was dissolved in TFA (5 mL) at rt, and the solution was stirred. After 3.5 h, the solution was concentrated under vacuum. Ether (100 mL) was added, and the solution was washed with $NaHCO_3$ (1 × 25 mL) and brine (1 × 25 mL). The organic layer was dried over Na_2SO_4 and concentrated to give an oil. The crude product was purified by silica gel chromatography (Et_2O, then EtOAc) to give the desired product (0.071 g, 85%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30–1.46 (m, 1H), 1.46–1.56 (m, 2H), 1.56–1.76 (m, 2H), 1.77–1.90 (m, 3H), 1.90–2.02 (m, 1H), 2.15–2.29 (m, 1H), 2.36–2.47 (m, 1H), 2.56 (dd, J = 6.9, 15.0 Hz, 1H), 3.37 (dt, J = 7.2, 11.8 Hz, 1H), 3.62–3.76 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 23.2, 29.6, 34.8, 35.6, 38.0, 46.7, 58.7, 173.9; IR (neat) 2922, 1635 cm^{-1}. MS (EI) m/z: M$^+$ 153, 124, 96, 84, 70 (100), 55. HRMS m/z: calcd for $C_9H_{15}NO$, 153.1154; found, 153.1154.

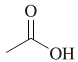
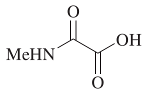
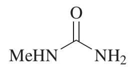
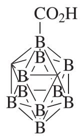
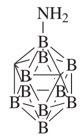
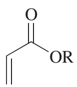
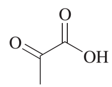
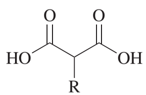
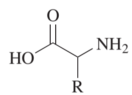
TABULAR SURVEY

The tables contain literature references for each of the Schmidt reaction variants discussed in this chapter. The coverage is from 1946 (when the previous *Organic Reactions* chapter on the Schmidt reaction was published)[11] to the end of 2009. In the tables, all carbon counts include protecting groups. The substrates are divided among the tables based on the reacting center, grouped by mechanism and oxidation state. For example, Table 1, “Schmidt Reactions of Carboxylic Acids with HN_3”, also includes esters and anhydrides. Compounds that contain both a reacting carboxylic acid and an acyclic ketone are placed in Table 3, "Schmidt Reactions of Acyclic Ketones with HN_3". Compounds that contain both a reacting cyclic and acyclic ketone are placed in Table 4, "Schmidt Reactions of Carbocyclic Ketones with HN_3". Table 5, "Schmidt Reactions of Heterocyclic Ketones with HN_3", only contains substrates in which the heterocyclic ketone is the reacting center, not just present in the molecule. Ketones that react via initial carbocation formation are placed in Tables 8 and 10, along with alcohols, alkenes, alkynes, and epoxides that react with a similar mechanism.

The following abbreviations are used in the tables:

BINOL	1,1′-bi(2-naphthol)
dppm	bis(diphenylphosphino)methane
eq	equivalent(s)
g	gas
MW	microwave irradiation
PNB	4-nitrobenzyl
s	secondary
t	tertiary

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 	NaN_3, H_2SO_4 or AcOH	$MeNH_2$ (89)	171
C_3 	NaN_3, H_2SO_4, PhH, 80°, 4 h	 (—)	172
	HN_3, H_2SO_4	 (—)	173
$C_{3–5}$ 	NaN_3, H_2SO_4, 40°, 17 h	 R: H (31); Me (32); Et (35)	80
$C_{3–9}$ 	1. HN_3, H_2SO_4, $CHCl_3$, 50°, 8 h 2. Amberlite IR-4B	 R: H (49); Me (83); Et (89); *n*-Pr (61); *i*-Pr (68); *n*-Bu (50); *s*-Bu (66); *t*-Bu (67); *n*-C_5H_{11} (54); *i*-C_5H_{11} (59); *n*-C_6H_{13} (38)	174

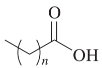
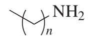
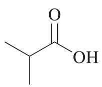
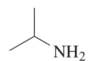
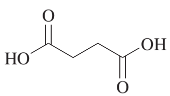
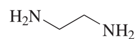
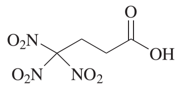
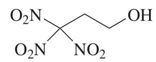
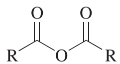
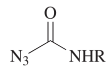
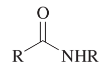
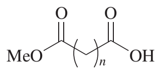
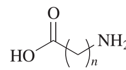
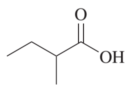
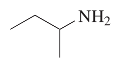
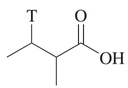
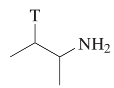
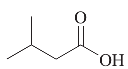
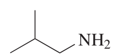
	Reactant	Conditions	Product(s) and Yield(s) (%)			Refs.
C_{3-18}						
		NaN_3, H_2SO_4, PhH, 50–60°		*n*		
				1	(—)	175–181
				2	(—)	177, 181, 177a, 179
				3	(—)	182
				4	(72)	183
				5	(—)	177
				6	(—)	182
				7	(—)	182
				8	(70)	184
				10	(81)	184, 182
				12	(80)	184
				14	(85)	184, 185
				16	(90)	184, 183
C_4						
		NaN_3, H_2SO_4, 40°	 (96)			171
		NaN_3, H_2SO_4	 (—)			186

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
	1. NaN_3, TFA 2. $NaNO_2$	 (88)	187
C_{4-10}			
	NaN_3, H_2SO_4, $CHCl_3$, 60°	 **I** +  **II** **I** + **II** (—) R: Me, *n*-Pr, *n*-Bu	188
C_{4-11}			
	1. HN_3, H_2SO_4, $CHCl_3$, 60° 2. H_2O, reflux	 *n* = 1 (58) *n* = 2 (79) *n* = 4 (74) *n* = 6 (—) *n* = 7 (81) *n* = 8 (83)	189 189 189 190 189 189
C_5			
	NaN_3, H_2SO_4, PhH, 50–60°	 (—)	175
	HN_3, H_2SO_4, $CHCl_3$	 (—)	191
	NaN_3, H_2SO_4	 (—)	192

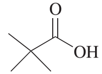
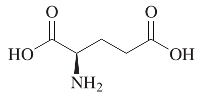
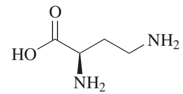
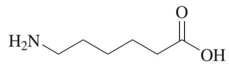
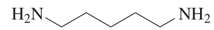
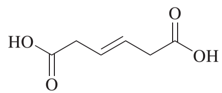
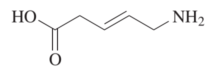
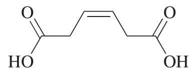
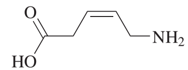
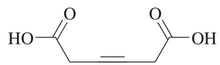
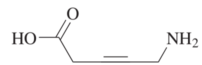
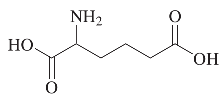
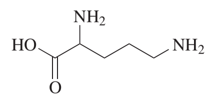
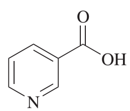
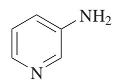
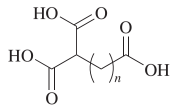
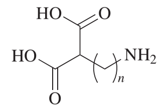
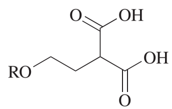
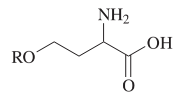
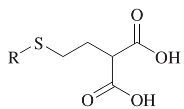
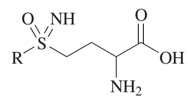
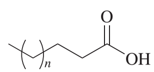
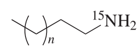
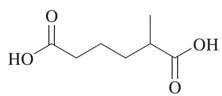
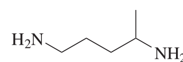
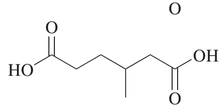
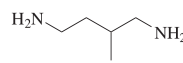
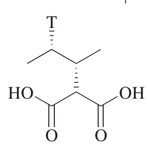
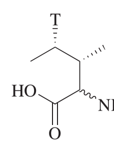
		NaN_3, H_2SO_4, 40°, 30 min	 (91)	193
		HN_3	 (—)	194
C_6		NaN_3, H_2SO_4, $CHCl_3$, 40°, 40 min	 (—)	195
		NaN_3, H_2SO_4, $CHCl_3$, 40°, 4 h	 (42)	168
		NaN_3, H_2SO_4, $CHCl_3$, 50°, 1 h	 (3)	168
		NaN_3, H_2SO_4, $CHCl_3$, 40°, 4 h	 (—)	168
		HN_3	 (77)	178
		NaN_3, 30% oleum, 95°, 6 h	 (69)	196

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-9} 	HN_3, H_2SO_4, $CHCl_3$, 60°, 2 h	 *n*: 2 (39); 3 (42); 4 (44); 5 (—)	197, 197, 197, 190
	HN_3, H_2SO_4, PhH, 50°, 3 h	 R: Me (23); Et (29); *n*-Pr (13); *n*-Bu (15)	198
	HN_3, H_2SO_4, PhH, 50°, 3 h	 R: Me (25); Et (29); *n*-Pr (25); *n*-Bu (30)	199
C_{6-18} 	$Na^{15}N_3$, PPA, 50°, 8 h	 *n*: 2 (72); 14 (98)	183
C_7 	HN_3	 (—)	200
	HN_3	 (83)	200
	HN_3, H_2SO_4, $CHCl_3$, rt to 55°, 4 h	 (34)	191

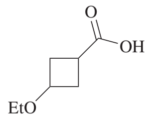
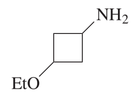
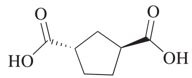
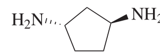
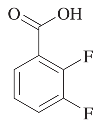
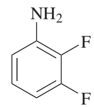
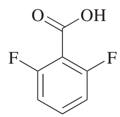
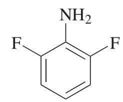
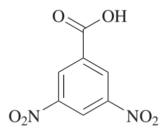
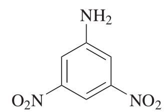
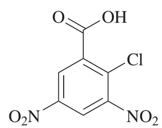
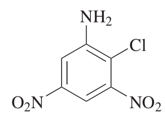
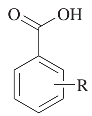
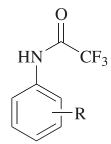
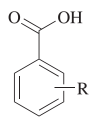
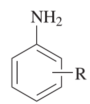
	HN_3		(—)	201
	NaN_3, H_2SO_4, $CHCl_3$, 60°, 4 h		(12)	202
	HN_3		(77)	203
	HN_3		(86)	203
	NaN_3, H_2SO_4, DCE, 80°, 3 h		(93)	204
	NaN_3, 20% oleum, DCE, 80°, 3 h		(92)	205

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.
C_{7-8} 	NaN_3, TFA, TFAA, 48 h		R			
			H	(72)		
			2-Br	(95)		206
			3-Br	(0)		
			4-Br	(0)		
			2-O_2N	(62)		
			3-O_2N	(0)		
			4-O_2N	(0)		
			2-Me	(87)		
			3-Me	(79)		
			4-Me	(71)		
C_{7-11} 	A: NaN_3, H_2SO_4, 40–50°, 2–12 h B: NaN_3, PPA, rt C: NaN_3, H_2SO_4, $CHCl_3$, rt, 2–24 h		R	Conditions		
			H	C	(97)	2
			2-F	A	(59)	207
			2-Cl	C	(80)	2
			2-Br	C	(73)	2
			2-I	C	(81)	2
			2-O_2N	C	(98)	2
			3-Cl	C	(71)	2
			3-Br	C	(70)	2
			3-O_2N	A	(100)	208
			4-F	A	(92)	208
			4-Cl	A	(99)	208
			4-Br	A	(96)	208

		$4\text{-}O_2N$	A	(99)	208
		2-Me	C	(86)	2
		3-Me	C	(84)	2
		4-Me	C	(50)	2
		4-NC	A	(73)	208
		$4\text{-}CF_3$	A	(41)	208
		4-MeO	B	(80)	161
		2-Et	C	(83)	2
		2-*i*-Pr	C	(87)	2
		2-*t*-Bu	C	(82)	2
		$2,4,6\text{-}Me_3$	B	(91)	161

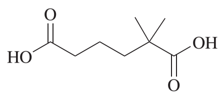
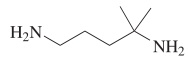
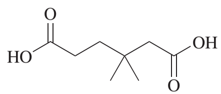
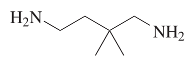
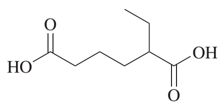
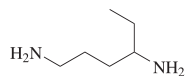
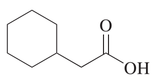
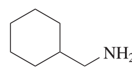
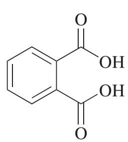
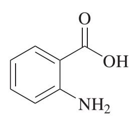
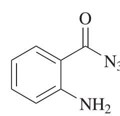
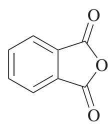
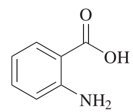
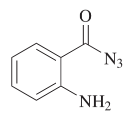
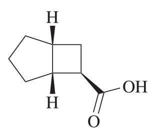
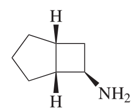
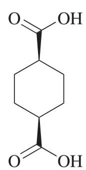
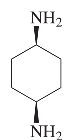
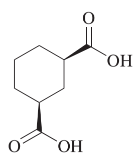
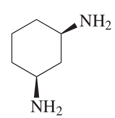
C_8		HN_3	 (—)	200
		HN_3	 (—)	200
		HN_3	 (—)	200
		NaN_3, H_2SO_4, $CHCl_3$, 55°, 12 h	 (86)	209
		NaN_3, H_2SO_4, DCE, 40°, 2 h	 (—) +  (37)	78

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	NaN_3, H_2SO_4, 110°, 30 min	 (73)	210
	NaN_3, AcOH, 50°, 3 h	 (12)	78
	HN_3	 (—)	211
	NaN_3, H_2SO_4, $CHCl_3$, 15–50°, 8 h	 (22)	212
	HN_3, H_2SO_4, $CHCl_3$, 15–50°, 8 h	 (44)	35, 213

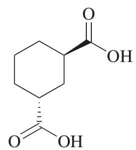
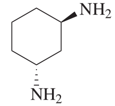
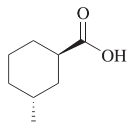
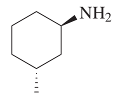
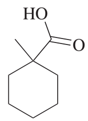
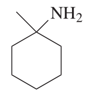
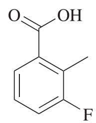
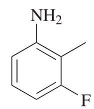
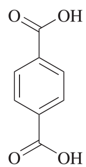
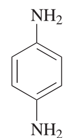
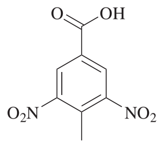
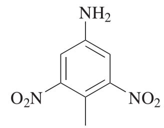
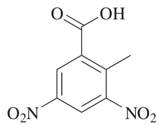
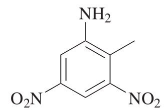
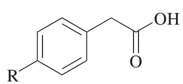
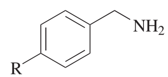
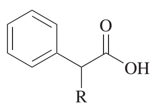
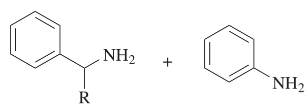
	HN_3, H_2SO_4, $CHCl_3$, 15–50°, 8 h	 (44)	35
	NaN_3, H_2SO_4, $CHCl_3$, 15–50°, 8 h	 (34)	214
	NaN_3, H_2SO_4, 55°, overnight	 (45)	209
	HN_3	 (76)	215
	NaN_3, H_2SO_4	 (—)	216

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	NaN_3, H_2SO_4, 0–60°, 4 h	 (90)	217
	NaN_3, H_2SO_4, 0–60°, 4 h	 (98)	217
C_{8-9} 	NaN_3, H_2SO_4, $CHCl_3$, 80°, 3 h	 R: O_2N (70); Cl (51); H (77); Me (5)	218
C_{8-12} 	NaN_3, PPA, 50°, 8 h	 **I** + **II**; R / **I** / **II**: H (68) (0); *n*-Bu (49) (46)	219

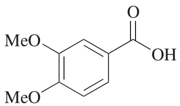
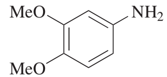
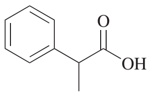
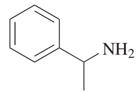
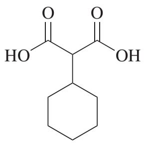
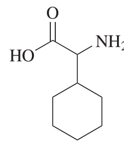
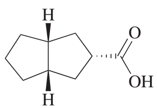
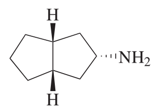
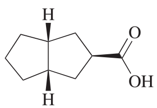
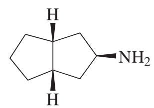
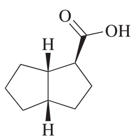
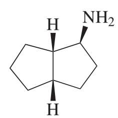
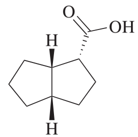
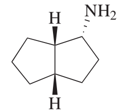
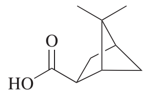
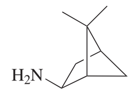
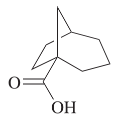
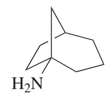
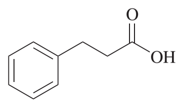
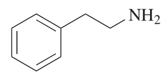
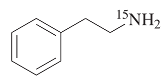
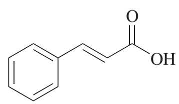
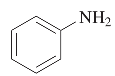
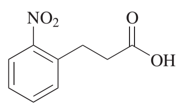
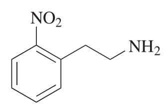
C_9				
	HN_3		(—)	220
	NaN_3, H_2SO_4, $CHCl_3$, rt to 45°, 1 h		(84)	221
	NaN_3, H_2SO_4, PhH, 50°, 5 h		(56)	222
	NaN_3, H_2SO_4, $CHCl_3$, 50°		(91)	223
	NaN_3, H_2SO_4, $CHCl_3$, 50°		(—)	224
	NaN_3, H_2SO_4, $CHCl_3$, 50°		(—)	225

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	NaN_3, H_2SO_4, $CHCl_3$, 50°	 (—)	226
	NaN_3, H_2SO_4, $CHCl_3$, 50°, 2 h	 (61)	227
	HN_3	 (63)	228
	NaN_3, H_2SO_4, $CHCl_3$, rt to 45°, 2 h	 (—)	229
	$Na^{15}N_3$, PPA, 50°	 (71)	183
	NaN_3, H_2SO_4	 (—)	230
	HN_3, H_2SO_4, $CHCl_3$, 45°	 (83)	231

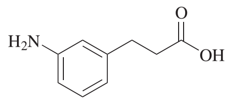
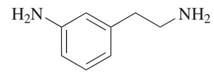
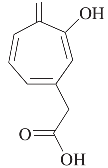
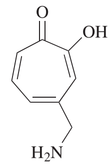
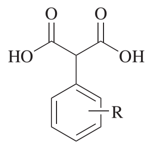
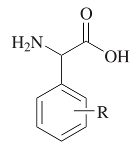
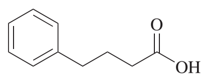
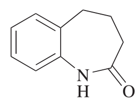
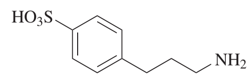
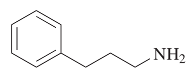
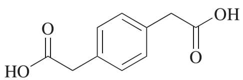
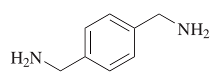
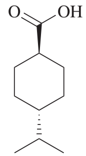
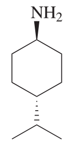
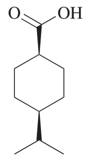
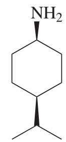
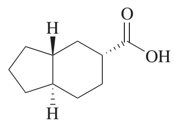
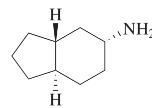
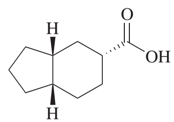
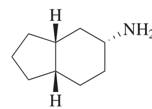
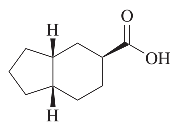
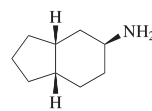
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	HN_3, H_2SO_4, $CHCl_3$, 45°	 (75)	231
	NaN_3, H_2SO_4, $CHCl_3$, 40°	 (70)	232
$C_{9–10}$ 	NaN_3, H_2SO_4, PhH, 50°, 5 h	 R: H (46); 2-Cl (27); 2-Br (30); 2-Me (38); 3-Me (50); 4-Me (0)	222
C_{10} 	NaN_3, H_2SO_4, $CHCl_3$, 40°, 1 h	 **I** (50) +  (40)	75
	NaN_3, PPA, 85°, 2 h	**I** (40) +  (24)	75
	NaN_3, H_2SO_4	 (—)	216

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	NaN_3, H_2SO_4, $CHCl_3$, 55°, 30 min	 (85)	233
	NaN_3, H_2SO_4, $CHCl_3$, 55°, 30 min	 (81)	233
	HN_3	 (—)	234
	HN_3	 (—)	234
	HN_3	 (—)	234

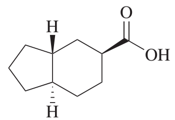
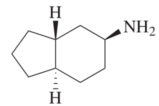
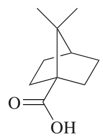
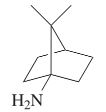
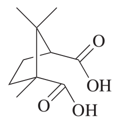
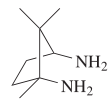
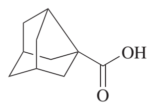
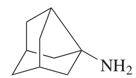
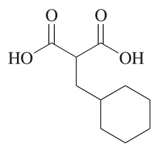
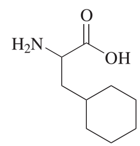
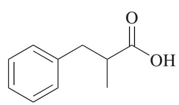
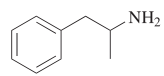
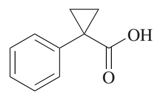
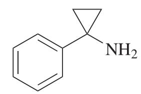
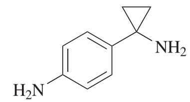
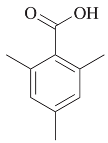
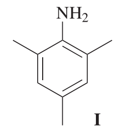
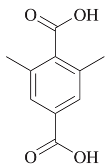
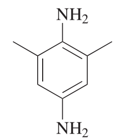
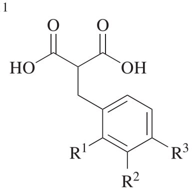
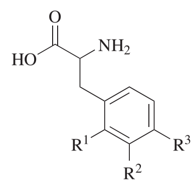
	HN_3	 (—)	234
	NaN_3, H_2SO_4, PhH, 50°, 2 h	 (—)	235
	NaN_3, H_2SO_4, $CHCl_3$, 55–65°, 1 h	 (76)	236
	NaN_3, H_2SO_4, $CHCl_3$, 45°, 2 h	 (63)	237
	NaN_3, H_2SO_4, PhH, 50°, 5 h	 (50)	222
	HN_3	 (—)	235

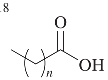
TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	NaN_3, H_2SO_4, $CHCl_3$, 80°, 3 h	 (16) +  (5)	218
	NaN_3, H_2SO_4, 0°	 **I** (51)	238
	NaN_3, PPA, rt	**I** (91)	161
	NaN_3, H_2SO_4, $CHCl_3$, rt	 (87)	238
C_{10-11} 	NaN_3, H_2SO_4, PhH, 50°, 5 h		222

R^1	R^2	R^3	
H	H	H	(19)
Cl	H	H	(37)
Br	H	H	(30)
I	H	H	(0)
H	Cl	H	(19)
H	Br	H	(20)
H	H	Cl	(36)
H	H	Br	(25)
H	H	I	(0)

H	H	O_2N	(32)
Cl	H	Cl	(22)
H	Cl	Cl	(21)
Me	H	H	(0)
MeO	H	H	(0)
H	H	Me	(0)

C_{10-18}



NaN_3, H_2SO_4, PhH, 50–60°

n		*n*	
8	(70)	14	(85)
10	(81)	16	(90)
12	(80)		

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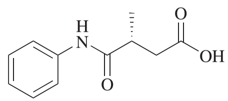
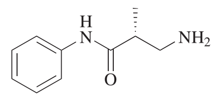
C_{11}

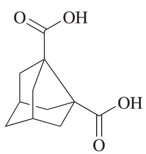


NaN_3, H_2SO_4, $CHCl_3$, 50°, 3 h

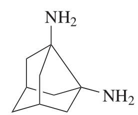


(32)

239



NaN_3, H_2SO_4, $CHCl_3$, 45°, 2 h



(13)

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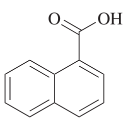
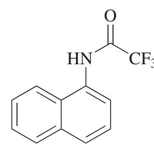


NaN_3, TFA/TFAA, 48 h



TFA/TFAA		TFA/TFAA	
10:0	(0)	4:6	(92)
9:1	(76)	3:7	(57)
8:2	(85)	2:8	(28)
7:3	(98)	1:9	(12)
6:4	(97)	0:10	(0)
5:5	(97)		

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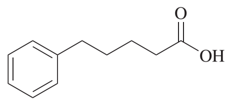
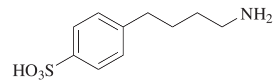
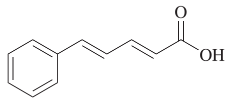
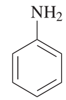
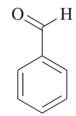
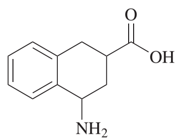
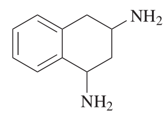
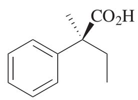
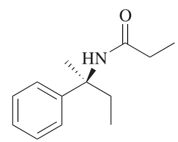
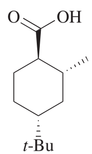
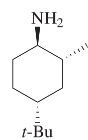
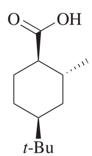
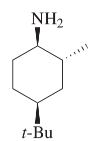
TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	NaN_3, H_2SO_4, $CHCl_3$, 40°, 1 h	 (80)	75
	HN_3, H_2SO_4, $CHCl_3$, 50°, 1 h	 (6) +  (13)	241
	NaN_3, $CHCl_3$, 45°, 20 h	 (55)	242
	1. NaN_3, MsOH, 0° to reflux 2. EtCOCl	 (64)	243
C_{12}			
	NaN_3, H_2SO_4, $CHCl_3$, 55°, 30 min	 (88)	233
	NaN_3, H_2SO_4, $CHCl_3$, 55°, 30 min	 (78)	244

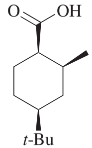
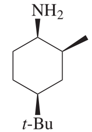
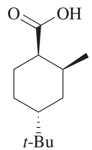
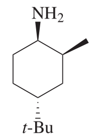
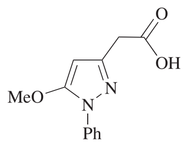
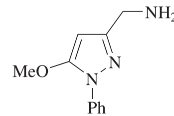
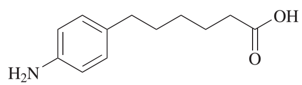
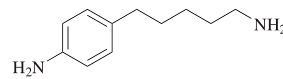
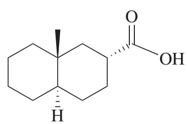
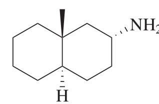
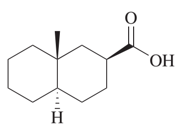
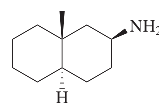
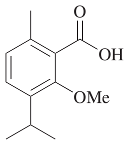
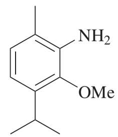
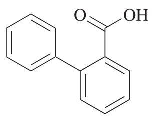
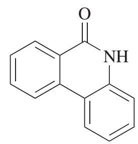
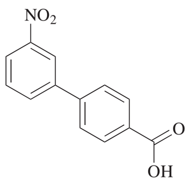
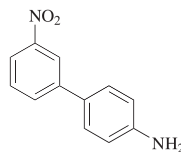
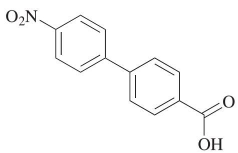
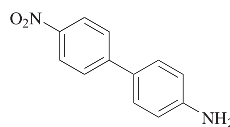
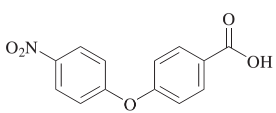
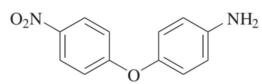
	NaN_3, H_2SO_4, $CHCl_3$, 55°, 30 min	 (66)	233
	NaN_3, H_2SO_4, $CHCl_3$, 55°, 30 min	 (78)	233
	HN_3, $CHCl_3$, 45°, 10 h	 (35)	245
	HN_3, H_2SO_4, $CHCl_3$, 45°	 (60)	231
	NaN_3, H_2SO_4, $CHCl_3$, 55°, 30 min	 (51)	233
	NaN_3, H_2SO_4, $CHCl_3$, 55°, 30 min	 (57)	233

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	HN_3, PhH, 40°, 1 h	 (48)	246
C_{13} 	NaN_3, H_2SO_4, $CHCl_3$	 (84)	218
	HN_3, 50°, 30 min	 (—)	247
	HN_3, 50°, 30 min	 (—)	247
	HN_3	 (—)	248

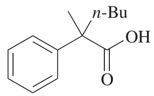
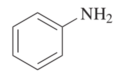
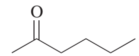
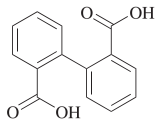
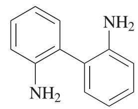
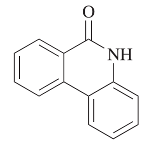
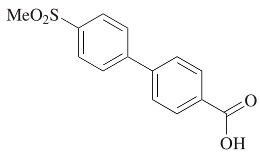
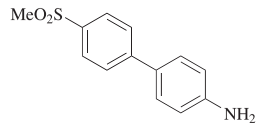
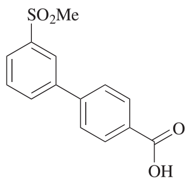
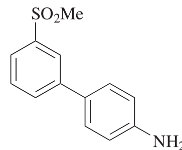
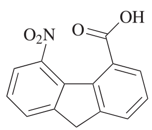
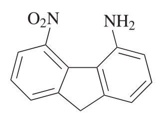
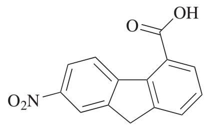
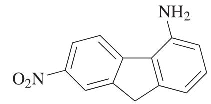
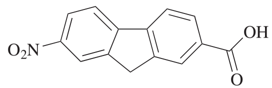
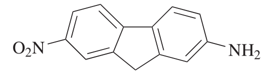
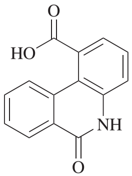
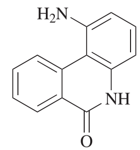
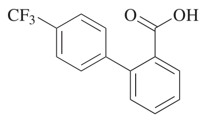
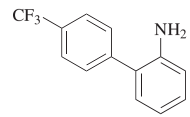
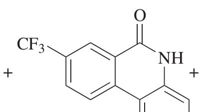
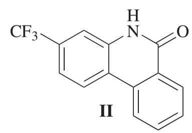
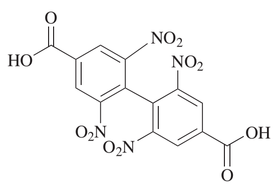
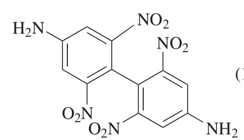
		NaN$_3$, PPA, 50°, 8 h	 (58)	+	 (—)	219
C_{14}		NaN$_3$, H$_2$SO$_4$, DCE, 40°, 2.5 h	 (43)	+	 (6)	78
		HN$_3$, 50°, 30 min	 (38)			247
		HN$_3$, 50°, 30 min	 (23)			247
		NaN$_3$, H$_2$SO$_4$, CHCl$_3$, 40°, 2 h	 (67)			249

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	NaN_3, H_2SO_4, $CHCl_3$, 40°, 2 h	 (70)	250
	NaN_3, H_2SO_4, $CHCl_3$	 (—)	251
	NaN_3, H_2SO_4, $CHCl_3$, 40°, 2 h	 (—)	252
	NaN_3, H_2SO_4, $CHCl_3$	 (22) +  **I** +  **II** **I + II** (21)	218
	NaN_3, DCE, reflux, 5 h	 (100)	253

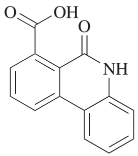
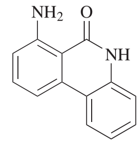
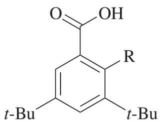
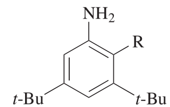
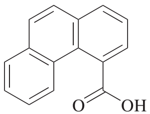
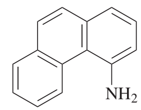
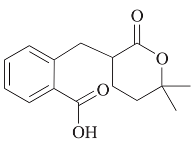
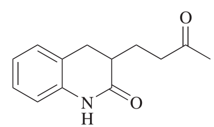
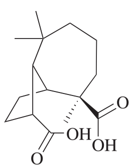
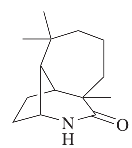
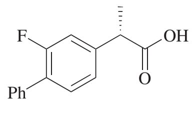
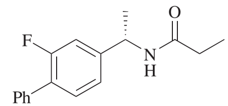
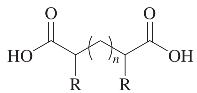
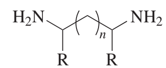
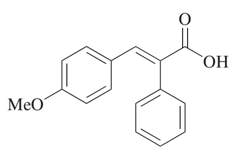
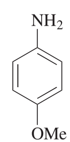
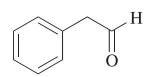
C_{15} 	NaN_3, H_2SO_4, $CHCl_3$	 (—)	254
	NaN_3, H_2SO_4, $CHCl_3$, rt	 R: H (86); O_2N (79); Cl (87); Br (90); I (96)	2; 2; 2; 2; 255
	1. NaN_3, TFA, TFAA 2. KOH	 (81)	256
	—	 (—) + CO_2	257
	HN_3, H_2SO_4, $CHCl_3$, rt, 1 h	 (96)	258

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	1. NaN_3, MsOH 2. EtCOCl	 (—)	243
C_{15-24}			
	NaN_3, H_2SO_4, PhH, rt	 *n* R 3 *n*-Bu (60) 3 *i*-Bu (75) 3 *n*-C_5H_{11} (78) 3 *i*-C_5H_{11} (80) 3 *n*-C_6H_{13} (75) 3 2-ethyl-1-hexyl (35) 4 *n*-Bu (60) 4 *n*-C_5H_{11} (60) 4 *i*-C_5H_{11} (76) 4 *n*-C_6H_{13} (80) 4 2-ethyl-1-hexyl (87) 5 *n*-Bu (79) 5 *i*-Bu (55) 5 *n*-C_6H_{13} (80)	259
C_{16}			
	HN_3, H_2SO_4, $CHCl_3$, 55°, 1 h	 (34) +  (35)	241

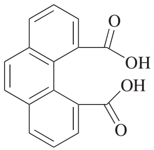
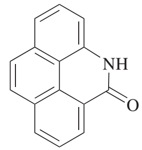
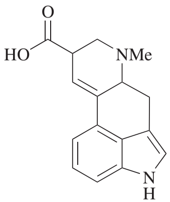
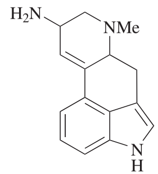
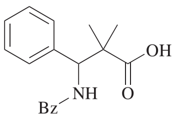
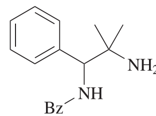
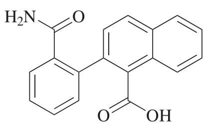
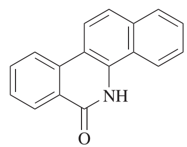
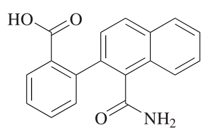
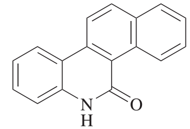
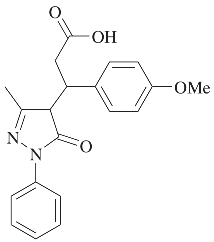
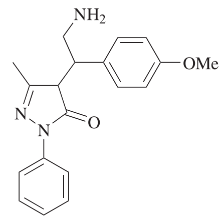
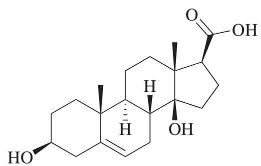
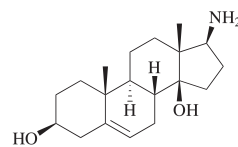
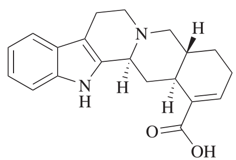
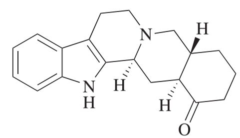
	NaN_3, H_2SO_4, DCE, 40°, 2.5 h	 (67)	78
	HN_3	 (—)	260
C_{18} 	NaN_3, H_2SO_4, $CHCl_3$, 55°, 1.5 h	 (41)	261
	NaN_3, H_2SO_4, 60°, 1 h	 (—)	262

TABLE 1. SCHMIDT REACTIONS OF CARBOXYLIC ACIDS WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}			
	NaN_3, H_2SO_4, 60°, 1 h	 (95)	262
C_{20}			
	NaN_3, H_2SO_4, $CHCl_3$, 0–50°, 5 h	 (64)	263
	HN_3	 (—)	264
	HN_3, H_2SO_4, $CHCl_3$	 (20)	265

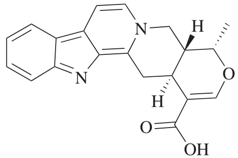
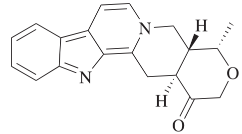
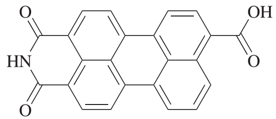
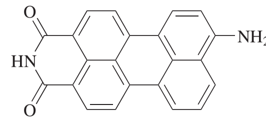
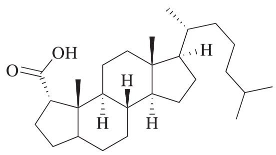
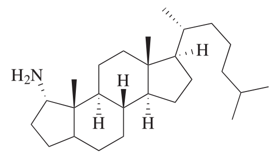
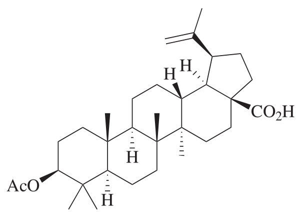
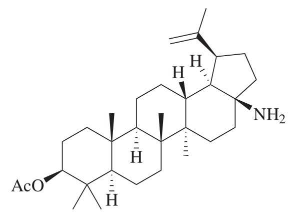
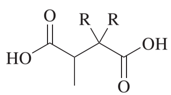
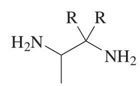
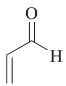
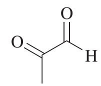
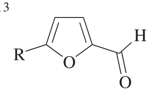
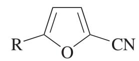
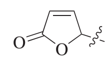
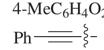
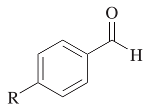
	HN_3	 (—)	266
C_{23}			
	NaN_3, H_2SO_4, 50°, 4 h	 (50)	267
C_{27}			
	NaN_3, H_2SO_4, $CHCl_3$	 (89)	106
	HN_3, PhH, 0° to rt	 (85)	268
C_{41}			
 R = n-$C_{18}H_{37}$	HN_3	 (—)	269

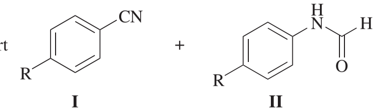
TABLE 2. SCHMIDT REACTIONS OF ALDEHYDES WITH HN_3

Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
C_3 	NaN_3, HCl, rt	 (37)			270
C_{5-13} 	HN_3, $Mg(ClO_4)_2$•H_2O, $CHCl_3$, reflux, 2 h		R		167
			H	(84)	
			Br	(88)	
			I	(85)	
			O_2N	(96)	
			Me	(91)	
			MeS	(79)	
			$ClCH_2$	(96)	
			$2-C_4H_3S$	(90)	
			EtO_2CCH_2S	(78)	
				(89)	
			$5-NC-2-C_4H_3S$	(92)	
			Ph	(90)	
			PhO_2S	(98)	
			$4-O_2NC_6H_4$	(85)	
			$4-ClC_6H_4O$	(81)	
			$2,4-(O_2N)_2C_6H_3S$	(93)	
			$4-MeC_6H_4O$	(79)	
			PhCOS	(90)	
			$3-BrC_6H_4COS$	(91)	
			$4-MeC_6H_4O_2S$	(98)	
				(94)	

C_{7-8}



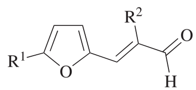
NaN_3, H_2SO_4 (x eq), PhH, 0° to rt



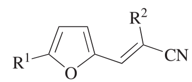
R	x	**I**	**II**
H	2	(32)	(14)
H	6.6	(10)	(59)
Cl	2	(55)	(12)
Cl	6.6	(15)	(48)
O_2N	2	(72)	(2)
O_2N	6.6	(46)	(23)
Me	2	(50)	(6)
Me	6.6	(13)	(43)
MeO	2	(86)	(0)
MeO	6.6	(64)	(0)

36

C_{7-14}



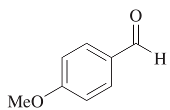
HN_3, $Mg(ClO_4)_2$•H_2O, $CHCl_3$, rt to reflux, 2 h



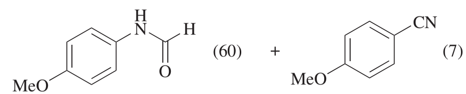
R^1	R^2	
H	H	(84)
H	Me	(92)
O_2N	H	(95)
Me	H	(92)
Me	Me	(82)
Ph	H	(95)
Ph	Me	(92)
2,4,6-$Cl_3C_6H_2$	H	(93)

271

C_8



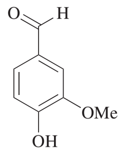
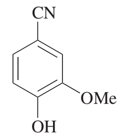
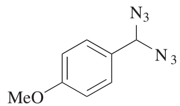
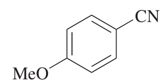
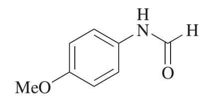
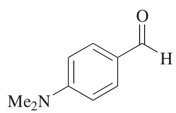
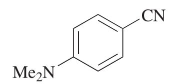
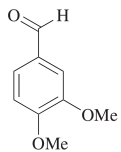
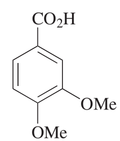
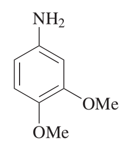
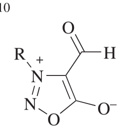
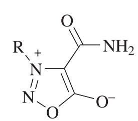
NaN_3, H_2SO_4, $CHCl_3$, 0–45°, 3 h



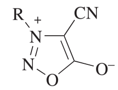
(60) + (7)

63

TABLE 2. SCHMIDT REACTIONS OF ALDEHYDES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	NaN_3, H_2SO_4, 0°, 2 h	 (70)	272
	H_2SO_4, MeCN	 (86) +  (2)	27
C_9 	NaN_3, H_2SO_4, 10°	 (61)	273
	NaN_3, H_2SO_4, 0°, 2 h	 (84) +  (6)	272
C_{9-10} 	NaN_3, H_2SO_4, rt, 10 h	 R: Ph (74); 4-BrC_6H_4 (63); 2-MeC_6H_4 (60); 4-MeC_6H_4 (68); 4-$MeOC_6H_4$ (47)	274

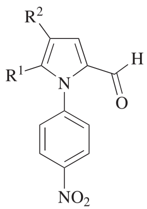
NaN$_3$, aq H_2SO_4, rt, 10 h



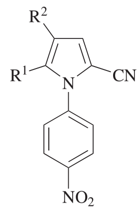
R	
Ph	(77)
4-BrC_6H_4	(67)
2-MeC_6H_4	(71)
4-MeC_6H_4	(73)
4-$MeOC_6H_4$	(72)

274

C_{11}



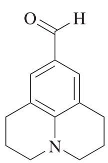
HN$_3$, $Mg(ClO_4)_2$•H_2O, $CHCl_3$, rt to reflux, 3 h



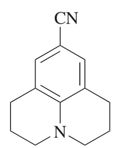
R^1	R^2	
H	H	(97)
Br	H	(98)
Br	Br	(98)

275

C_{13}



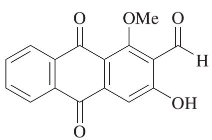
NaN$_3$, H_2SO_4, 10°



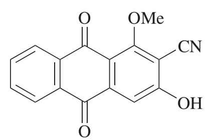
(77)

273

C_{16}



HN$_3$



(—)

276

TABLE 2. SCHMIDT REACTIONS OF ALDEHYDES WITH HN_3 (*Continued*)

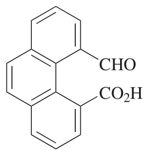
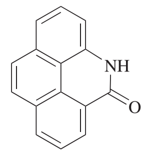
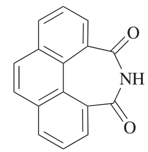
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	NaN_3, H_2SO_4, DCE, 40°, 2.5 h	 (—) +  (—)	78

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3

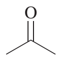
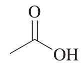
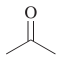
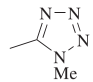
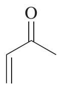
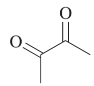
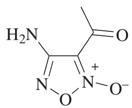
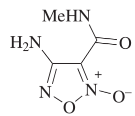
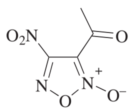
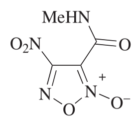
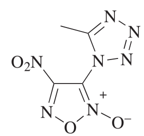
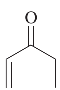
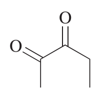
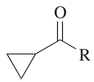
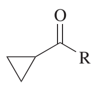
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3			
	NaN_3, H_2SO_4, PhH	 (—) + $MeNH_2$ (—)	277
	$SiCl_4$, NaN_3, MeCN, rt, 12 h	 (98)	70
C_4			
	NaN_3, HCl, rt	 (8)	270
	NaN_3, PPA, rt, 48 h	 (21)	278
	NaN_3, PPA, rt, 48 h	 (12) +  (12)	278
C_5			
	NaN_3, HCl, rt	 (50)	270

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-10} 	A: NaN_3, 89% H_2SO_4, $CHCl_3$ B: NaN_3, 83% H_2SO_4, $CHCl_3$ C: NaN_3, 69% H_2SO_4, $CHCl_3$ D: NaN_3, 50% H_2SO_4, $CHCl_3$ E: NaN_3, CCl_3CO_2H, 63°	 **I** + **II**	30

R	Conditions	**I + II**	**I:II**
Me	A	(88–100)	73:27
Me	B	(88–100)	74:26
Me	C	(88–100)	44:56
Me	D	(—)	10:90
Me	E	(88–100)	27:73
Et	B	(88–100)	82:18
Et	C	(88–100)	82:18
Et	D	(—)	26:74
Et	E	(88–100)	26:74
i-Pr	B	(88–100)	92:8
i-Pr	C	(88–100)	96:4
i-Pr	D	(—)	82:18
i-Pr	E	(88–100)	48:52
Ph	A–C, E	(88–100)	7:93

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-12} 	NaN_3, H_2SO_4, $CHCl_3$, rt	**I + II**	279

R	**I + II**	**I:II**
Me	(75)	1:3.3
Ph	(76)	1:19
2-MeC_6H_4	(85)	1:19
4-MeC_6H_4	(61)	1:19
(*E*)-PhCH=CH	(35)	1:10

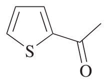
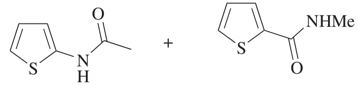
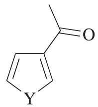
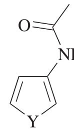
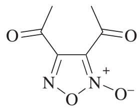
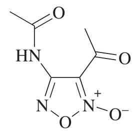
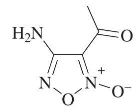
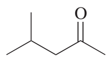
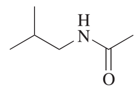
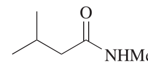
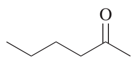
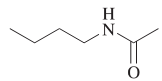
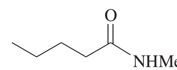
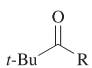
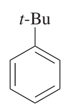
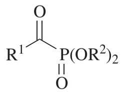
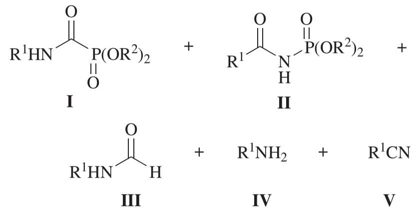
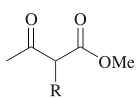
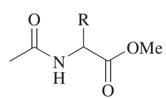
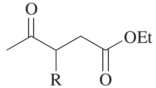
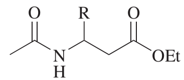
C_6 	HN_3, H_2SO_4, $CHCl_3$, 0°, 15 min	 I + II I + II (—)	280
	HN_3, H_2SO_4, $CHCl_3$, 0°, 15 min	 Y: O (20); S (80); Se (75)	281
	NaN_3, H_2SO_4, CH_2Cl_2, 0°, 3 h	 (—) +  (63)	278
	NaN_3, silica sulfuric acid,[a] 60°, 20 min	 (66) +  (26)	282
	NaN_3, silica sulfuric acid,[a] 60°, 20 min	 (69) +  (23)	282
$C_{6–9}$ 	NaN_3, H_2SO_4, PhH, rt	 I + t-BuNH$_2$ II; R = Me: I (30), II (3); R = t-Bu: I (23), II (9)	283

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

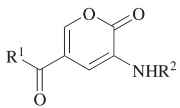
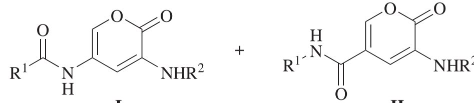
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-14} 	HN_3, H_2SO_4, $CHCl_3$, 0°, 30 min		28
	NaN_3, MsOH, DME, –30° to rt, 3 h		56

R^1	R^2	I	II	III	IV	V
i-Pr	Me	(0)	(0)	(57)	(0)	(0)
3-ClC_6H_4	Me	(0)	(1)	(39)	(7)	(0)
4-$MeOC_6H_4$	Me	(0)	(46)	(0)	(0)	(47)
4-$MeOC_6H_4$[b]	Me	(0)	(45)	(0)	(0)	(51)
Ph	Et	(9)	(3)	(53)	(14)	(0)
4-ClC_6H_4	Et	(19)	(2)	(65)	(4)	(0)
4-MeC_6H_4	Et	(11)	(3)	(70)	(7)	(7)
4-$MeOC_6H_4$	Et	(0)	(30)	(0)	(0)	(62)
4-$MeOC_6H_4$[c]	Et	(0)	(31)	(0)	(0)	(54)
3-$MeOC_6H_4$	Et	(0)	(2)	(59)	(9)	(6)
3,4-$(OCH_2O)C_6H_3$	Et	(0)	(28)	(0)	(0)	(51)
2,6-$(MeO)_2C_6H_3$	Et	(0)	(0)	(0)	(0)	(62)
2,4,6-$Me_3C_6H_2$	Et	(0)	(0)	(0)	(43)	(0)
2,6-Me_2-4-$MeOC_6H_2$	Et	(0)	(0)	(0)	(50)	(0)

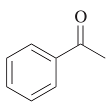
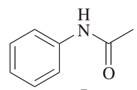
R	
Me	(47)
Bn	(26)
$Ph(CH_2)_2$	(100)
(*E*)-PhCH=$CHCH_2$	(79)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-14} 	NaN_3, H_2SO_4, $CHCl_3$, 5°		284

R	
H	(49)
Me	(70)
Et	(29)
Bn	(19)

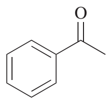
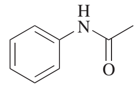
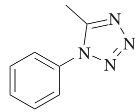
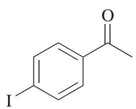
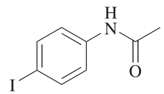
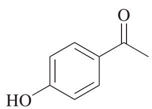
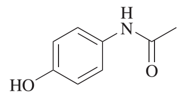
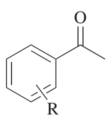
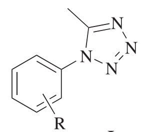
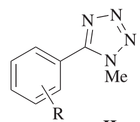
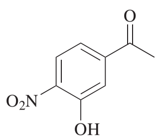
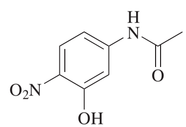
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-19} 	A: NaN_3, H_2SO_4, –10 to 0°, 3 h; then rt, 2 h B: NaN_3, H_2SO_4, 32–35°, 2 h	 **I** + **II**	285

R^1	R^2	Conditions	**I + II**	**I:II**
Me	H	A	(96)	1:0
Me	H	B	(86)	1:0
Me	MeCO	A	(86)	1:0
Me	PhCO	A	(98)	1:0
Ph	H	A	(87)	3.9:1
Ph	H	B	(92)	3.6:1
Ph	MeCO	A	(72)	3.7:1
Ph	PhCO	A	(99)	3.5:1

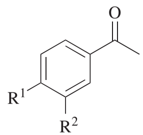
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	NaN_3, MsOH, DME, –30° to rt, 3 h	 **I** (80)	56
	NaN_3, AcOH, HBr, 55–65°	**I** (21)	1
	NaN_3, CCl_3CO_2H, 55–65°	**I** (89)	1
	Azide, $FeCl_3$, DCE, rt	**I**	286

Azide	Time	
$TMSN_3$	30 min	(85)
NaN_3	2 h	(76)

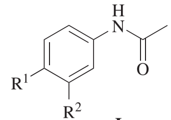
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	NaN_3, PPA, 50°, 7 h	 (82)	54
	HN_3, $AlCl_3$, $PhNO_2$, PhH, rt	 (42)	272
	Azide, $FeCl_3$, DCE, rt	 Azide / Time $TMSN_3$ 35 min (76) NaN_3 3 h (68)	286
	Azide, $FeCl_3$, DCE, rt	 Azide / Time $TMSN_3$ 33 min (72) NaN_3 2.5 h (66)	286
	NaN_3, $SiCl_4$, MeCN, rt, 12 h	 **I** +  **II** R / **I** / **II** H (87) (5) 4-Cl (87) (5) 3-O_2N (60) (5)	70
	NaN_3, MsOH, rt, 14 h	 (82)	287

C_{8-9}

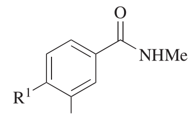


A: NaN_3, H_2SO_4, PhH, 60°
B: NaN_3, CCl_3CO_2H, 65°



I

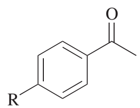
+



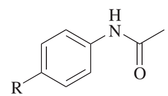
II

I + **II** (—) 59

R^1	R^2	Conditions	**I:II**
H	H	A	90:10
H	H	B	90:10
O_2N	H	A	90:10
O_2N	H	B	90:10
H	O_2N	A	90:10
H	O_2N	B	90:10
MeO	H	A	80:20
MeO	H	B	80:20



NaN_3, silica sulfuric acid,[a] 60°



I

R	Time (min)	
H	25	(95)
Cl	35	(92)
O_2N	45	(90)
Me	25	(91)

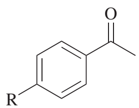
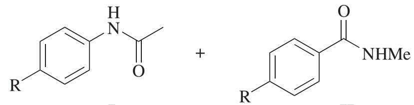
282

NaN_3, $Fe(HSO_4)_3$, grinding, 50° **I**

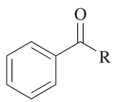
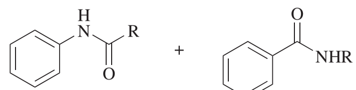
R	Time (min)	
H	25	(92)
Cl	35	(91)
O_2N	25	(91)
Me	35	(94)

288

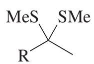
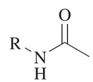
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 	NaN_3, P_2O_5–SiO_2, MW	 I + II	289

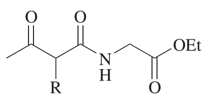
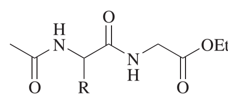
R	Time (min)	**I + II**	**I:II**
H	8	(90)	1:0
Cl	8	(90)	1:0
O_2N	10	(80)	4:1
Me	10	(85)	1:0
MeO	10	(83)	1:0

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-10} 	NaN_3, HCl (concd)	 I + II	7

R	**I + II**	**I:II**
Me	(81)	95:6
Et	(80)	85:15
i-Pr	(57)	51:49

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. IN_3, CH_2Cl_2, –78 to –10°, 2 h 2. TFA, $CHCl_3$, rt, 2 h		83

R	
t-Bu	(62)
n-C_5H_{11}	(77)
c-C_6H_{11}	(59)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-15} 	HN_3, H_2SO_4		290

R	
H	(49)
Me	(56)
Et	(57)
n-Pr	(50)
n-Bu	(34)
Bn	(82)

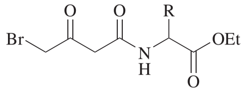
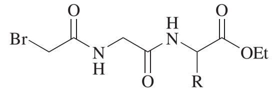
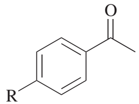
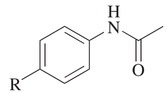
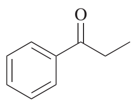
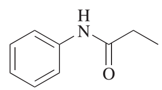
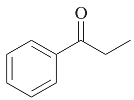
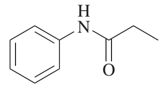
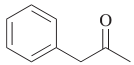
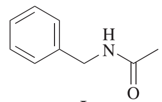
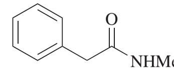
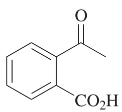
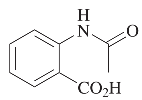
Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
	HN_3, H_2SO_4		R		
			H	(35)	291
			Bn	(21)	
C_{8-20}					
	A. NaN_3, AcOH, H_2SO_4, 70°, 2–6 h B. NaN_3, H_2SO_4		R	Conditions	
			H	A (99)	292
			O_2N	A (70)	292
			n-C_5H_{11}	A (81)	293
			Ph	A (99)	292
			PhO	A (99)	292
			PhS	A (99)	292
			PhOS	A (60)	292
			PhO_2S	A (85)	292
			4-$O_2NC_6H_4$	A (80)	292
			4-$O_2NC_6H_4O$	A (50)	292
			n-C_5H_{11}	B (81)	294
			Bn	A (70)	292
			n-C_7H_{15}	B (—)	294
			n-C_9H_{19}	B (—)	294
			n-$C_{10}H_{21}$	A (93)	293
			n-$C_{12}H_{25}$	A (95)	293
C_9					
	NaN_3, silica sulfuric acid,[a] 60°, 0.5 h	 **I** (95)			282
	NaN_3, P_2O_5–SiO_2, MW, 8 min	**I** (92)			289
	NaN_3, $Fe(HSO_4)_3$, 50°, 30 min	**I** (93)			288

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	Azide, $FeCl_3$, DCE, rt	 Azide / Time: $TMSN_3$, 35 min (78); NaN_3, 2 h (70)	286
	NaN_3, promoter	 **I** +  **II**	
	NaN_3, CCl_3CO_2H, 60°	 (65)	8

Promoter	Solvent	Temp	Time (h)	**I + II**	**I:II**	Refs.
PPA	PPA	rt	8	(43)	100:0	295
H_2SO_4	Et_2O	0°	3	(—)	31:69	296
H_2SO_4	Et_2O	rt	3	(—)	40:60	296
H_2SO_4	PhH/Et_2O (1:9)	rt	3	(—)	44:56	296
H_2SO_4	PhH/Et_2O (1:1)	rt	3	(—)	64:36	296
H_2SO_4	PhH/Et_2O (9:1)	rt	3	(—)	78:22	296
H_2SO_4	PhH	0°	3	(—)	80:20	296
H_2SO_4	PhH	rt	3	(—)	79:21	296
PPA	PPA	20°	5	(—)	76:24	296
PPA	PPA	50°	3	(—)	72:28	296
PPA	PPA	100°	1	(—)	67:23	296
silica sulfuric acid[a]	—	60°	0.4	(91)	75:25	282
P_2O_5–SiO_2	—	MW	0.17	(91)	75:25	289
$Fe(HSO_4)_3$	—	50°	0.4	(90)	80:20	288

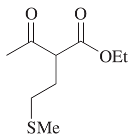
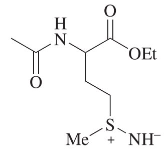
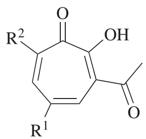
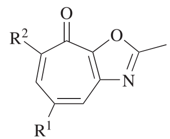
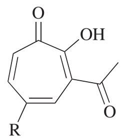
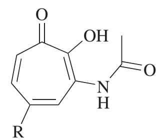
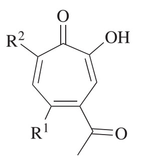
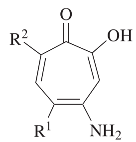
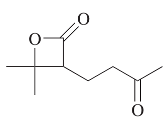
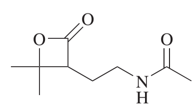
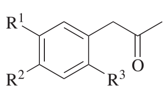
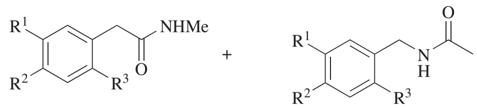
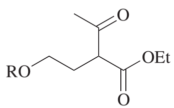
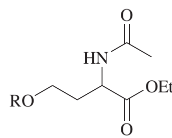
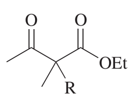
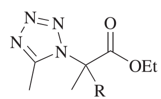
	HN_3, H_2SO_4, $CHCl_3$, PhH	 (—)	297
	NaN_3, H_2SO_4, $CHCl_3$, rt, 2 h	 R^1 / R^2: H / I (39); Br / Br (69)	298
	NaN_3, H_2SO_4, $CHCl_3$, rt, 2 h	 R: H (66); O_2N (47)	299, 298
	NaN_3, H_2SO_4, $CHCl_3$, rt, 2 h	 R^1 / R^2: H / H (94); Br / H (—); H / O_2N (83); Br / O_2N (—)	300
	HN_3, H_2SO_4, $CHCl_3$	 (70)	301

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10} 	A: NaN_3, PPA, 0°, 6 h B: NaN_3, H_2SO_4, PhH, rt, 6 h C: NaN_3, H_2SO_4, Et_2O, 0°, 6 h	 **I** + **II**	296
C_{9-12} 	HN_3, H_2SO_4, PhH, 50°, 3 h		198
C_{9-14} 	$TMSN_3$, $ZnBr_2$, 65°, 24 h		302

R^1	R^2	R^3	Conditions	**I** + **II**	**I**:**II**
H	H	H	A	(>95)	24:76
H	H	H	B	(>95)	20:80
H	H	H	C	(>95)	60:40
H	H	O_2N	A	(90)	27:73
H	H	O_2N	B	(100)	14:86
H	H	O_2N	C	(40)	67:33
H	O_2N	H	A	(90)	15:85
H	O_2N	H	B	(100)	14:86
H	O_2N	H	C	(60)	33:67
—OCH_2O—		H	A	(35)	90:10
—OCH_2O—		H	B	(—)	—
—OCH_2O—		H	C	(29)	43:57

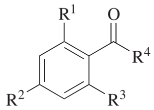
C_{9-12} product:

R	
Me	(85)
Et	(90)
n-Bu	(82)

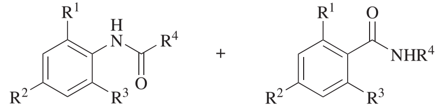
C_{9-14} product:

R	
Et	(90)
i-Bu	(78)
Ph	(40)
Bn	(70)

C_{9-19}



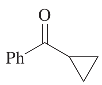
NaN_3, H_2SO_4, CCl_3CO_2H, 60°, 1–5 h



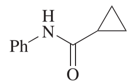
I + **II** (8)

R^1	R^2	R^3	R^4	**I + II**	**I:II**
Me	H	H	Me	(—)	99:1
HO_2C	H	H	Me	(65)	91:9
Cl	H	H	Ph	(100)	30:70
Br	H	H	Ph	(100)	19:81
O_2N	H	H	Ph	(—)	70:30
Me	H	H	Ph	(34)	12:88
MeO	H	H	Ph	(88)	50:50
HO_2C	H	H	Ph	(—)	98:2
Me	Me	Me	Ph	(—)	95:5
Ph	H	H	Ph	(35)	95:5

C_{10}

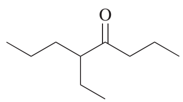


Azide, $FeCl_3$, DCE, rt

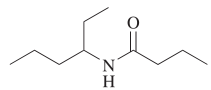
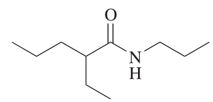


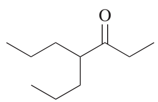
Azide	Time	
$TMSN_3$	45 min	(81)
NaN_3	3.5 h	(73)

286



NaN_3, H_2SO_4, $CHCl_3$

 (—) +  (—) 303



NaN_3, H_2SO_4, $CHCl_3$

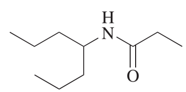
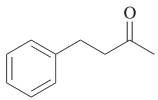
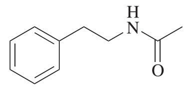
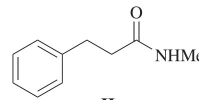
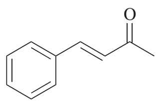
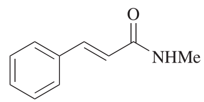
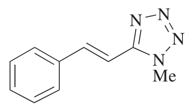
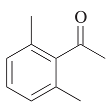
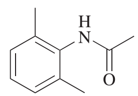
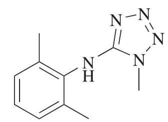
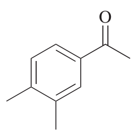
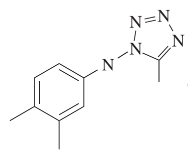
 (—) 303

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	NaN_3, PPA, rt, 8 h	 **I** (95) +  **II** (—)	54
	NaN_3, silica sulfuric acid,[a] 60°, 45 min	**I + II** (93), **I**:**II** = 5:1	282
	NaN_3, P_2O_5, SiO_2, MW, 10 min	**I + II** (93), **I**:**II** = 5:1	289
	NaN_3, $Fe(HSO_4)_3$, 50°, 25 min	**I + II** (90), **I**:**II** = 4:1	288
	NaN_3, PPA, rt, 8 h	 (58)	54
	$SiCl_4$, NaN_3, MeCN, rt, 12 h	 (95)	70
	NaN_3, H_2SO_4, 0° to rt, 14 h	 (—) +  (—)	304
	NaN_3, H_2SO_4	 (72)	305

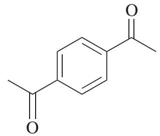
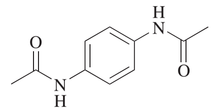
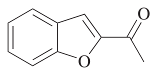
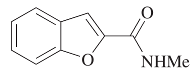
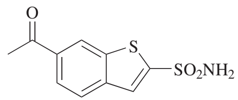
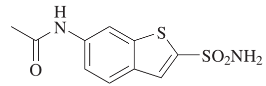
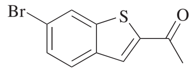
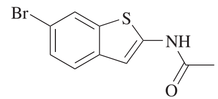
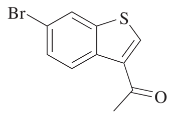
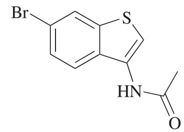
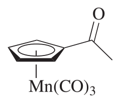
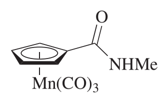
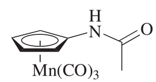
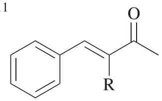
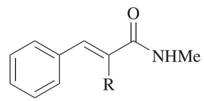
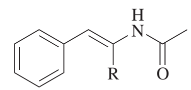
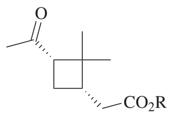
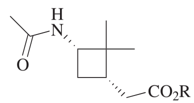
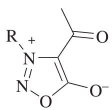
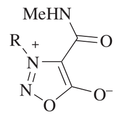
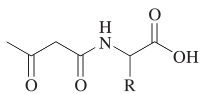
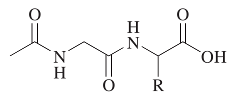
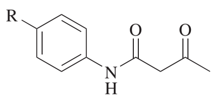
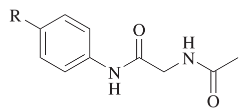
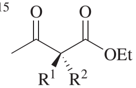
	NaN_3, H_2SO_4, $CHCl_3$	 (—)		216
	NaN_3, CCl_3CO_2H, $CHCl_3$, 50°, 3 h	 (80)		69
	NaN_3, AcOH, H_2SO_4, 80°, 3 h	 (28)		306
	HN_3, AcOH, 95°, 8 h	 (74)		307
	HN_3, AcOH, 95°, 8 h	 (70)		307
	NaN_3, PPA, 65°, 19 h	 **I** +  **II**	**I** + **II** (73), **I**:**II** = 3:2	308, 309
	NaN_3, H_2SO_4	**I** + **II** (12), **I**:**II** = 3:2		308, 309
	NaN_3, TFA	**I** + **II** (50), **I**:**II** = 3:2		308, 309

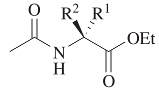
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-11}			
	NaN_3, CCl_3CO_2H	 **I** +  **II** R / **I** / **II** H (75) (0) Me (0) (86)	7
C_{10-12}			
	HN_3, H_2SO_4, $CHCl_3$	 R H (89) Et (92)	301
	NaN_3, H_2SO_4, 0° to rt, 6 h	 R Ph (50) 4-BrC_6H_4 (74) 4-MeC_6H_4 (77) 4-$MeOC_6H_4$ (58) 4-$EtOC_6H_4$ (63)	310
C_{10-13}			
	HN_3, H_2SO_4	 R *i*-Bu (48) Bn (46)	290
	NaN_3, H_2SO_4, $CHCl_3$	 R H (57) H_2NO_2S (44) $(HO)_2AsO$ (70) EtO (35) EtO_2C (50)	311

C$_{10-15}$

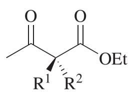


NaN_3, MsOH, HCl, 0° to reflux, 6 h

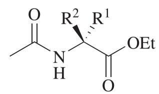


R^1	R^2		Refs.
allyl	Me	(44)	109
n-Pr	Me	(99)	109
i-Pr	Me	(50)	109
n-Bu	Me	(89)	109
i-Bu	Me	(80)	109
allyl	Et	(0)	109
n-Pr	Et	(48)	109
i-Pr	Et	(21)	109
n-Bu	Et	(37)	109
i-Bu	Et	(35)	312
Et	*i*-Bu	(40)	109
H	Bn	(90)	313
Bn	Me	(95)	109
Bn	Et	(52)	109

C$_{10-20}$

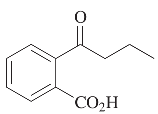


A. NaN_3, MsOH, $CHCl_3$, reflux, 1 h
B. NaN_3, H_2SO_4, DME, rt, 24 h

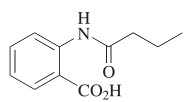


R^1	R^2	Conditions		Refs.
MeO_2CCH_2	Me	A	(88)	108
Bn	Me	A	(95)	108
Bn	Me	B	(82)	314
4-$BrC_6H_4CH_2$	Me	B	(63)	314
4-$BrC_6H_4CH_2$	Bu	B	(43)	314
2-$C_{10}H_7CH_2$	Me	A	(89)	108
2-$C_{10}H_7CH_2$	Me	B	(82)	314
2-$C_{10}H_7CH_2$	Bu	B	(41)	314

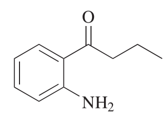
C$_{11}$



NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h

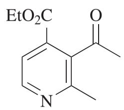
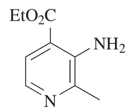
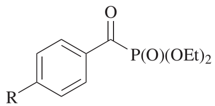
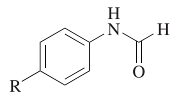
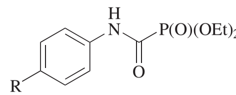
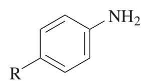
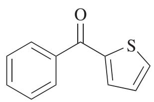
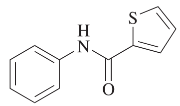
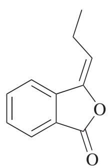
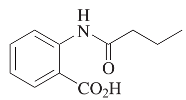
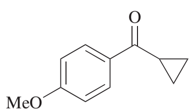
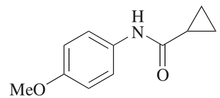


(77) +



(5) 315

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		1. NaN_3, H_2SO_4, $CHCl_3$, rt, 18 h 2. H_2O, reflux, 1.5h	 (94)	316
		HN_3, H_2SO_4, $CHCl_3$	 **I** +  **II** +  **III** R | **I** | **II** | **III** H | (53) | (9) | (14) Cl | (65) | (19) | (0)	82
		NaN_3, H_2SO_4, CCl_3CO_2H, 50°, 3 h	 (49)	317
		NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h	 (69)	315
		Azide, $FeCl_3$, DCE, rt	 Azide | Time | $TMSN_3$ | 49 min | (78) NaN_3 | 3.5 h | (70)	286

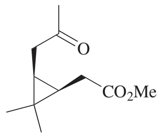
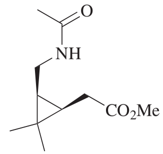
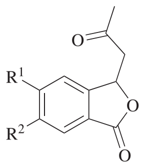
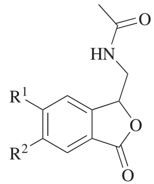
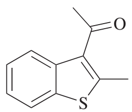
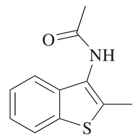
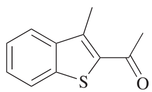
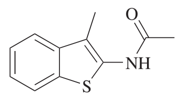
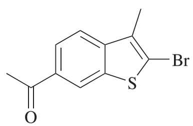
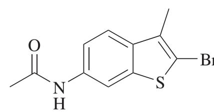
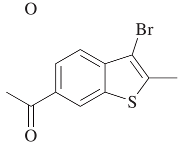
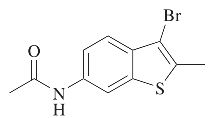
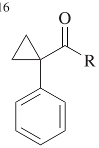
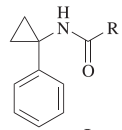
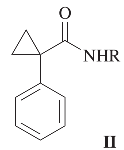
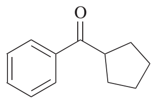
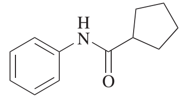
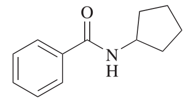
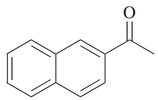
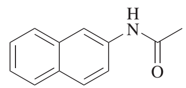
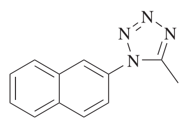
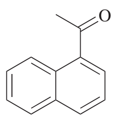
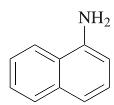
	NaN_3, MsOH, DME, –30° to rt	 (68)	318
	NaN_3, PPA, 20–90°, 4 h	 R^1 R^2 H H (40) Cl H (—) Cl Cl (80)	319
	HN_3, AcOH, 70°	 (82)	320
	HN_3, AcOH, 70°	 (50)	320
	HN_3, AcOH, 70°	 (63)	320
	HN_3, AcOH, 70°	 (71)	320

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-16} 	NaN_3, H_2SO_4, $CHCl_3$, rt	 **I** +  **II** R — **I + II** — **I:II** Me — (81) — 3.3:1 Ph — (66) — 1.7:1	279
C_{12} 	NaN_3, $ClCH_2CO_2H$, 60°, 6 h	 (—) +  (—)	321
	NaN_3, MsOH, DME, –30° to rt, 3 h	 **I** (91)	56
	NaN_3, PPA, 55°, 12 h	**I** (81)	54
	NaN_3, CCl_3CO_2H, 60°	**I** (95)	1
	NaN_3, H_2SO_4	**I** (55)	1
	NaN_3, $POCl_3$, $CHCl_3$	**I** (42)	1
	NaN_3, $AlCl_3$, $PhNO_2$	 (73)	1
	1. NaN_3, x% H_2SO_4, 0°, 8 h 2. HCl, EtOH, reflux, 24 h	 x — yield 75 — (15) 85 — (48) 90 — (70) 95 — (36)	5

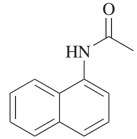
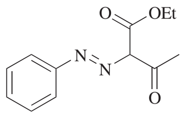
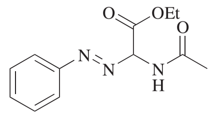
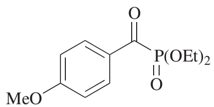
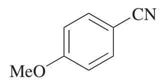
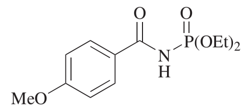
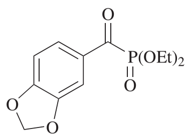
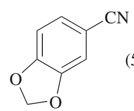
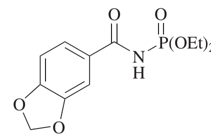
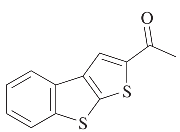
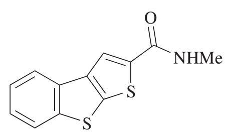
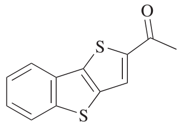
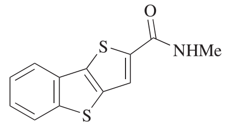
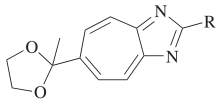
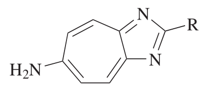
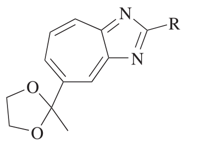
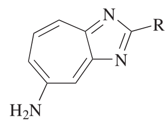
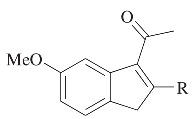
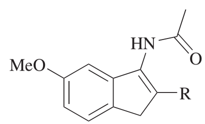
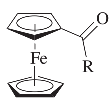
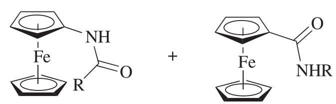
	NaN_3, PPA, 55°, 12 h	 **I** (72)	54
	NaN_3, CCl_3CO_2H, 60°	**I** (90)	1
	NaN_3, H_2SO_4, $CHCl_3$, 0–55°	 (71)	322
	HN_3, H_2SO_4, $CHCl_3$	 (65) +  (30)	82
	HN_3, H_2SO_4, $CHCl_3$	 (57) +  (28)	82
	NaN_3, H_2SO_4, AcOH, 100°, 8 h	 (67)	323

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	NaN_3, H_2SO_4, AcOH, 100°, 8 h	 (60)	323
	NaN_3, H_2SO_4, rt, 2 h	 R / H (—) / H_2N (80)	324
$C_{12–13}$			
	NaN_3, H_2SO_4, rt, 2 h	 (—) R / H / H_2N / MeS	324
	NaN_3, TFA, $CHCl_3$, 60°, 4 h	 R / H (78) / Me (80)	69
$C_{12–17}$			
	NaN_3, PPA, 60°, 28 h	 **I** + **II**; R, I, II / Me (20) (10) / Ph (10) (5)	309

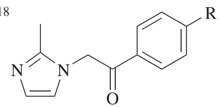
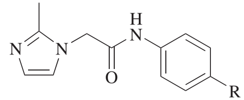
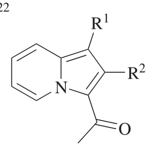
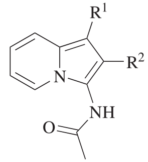
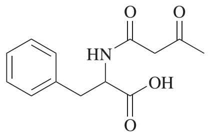
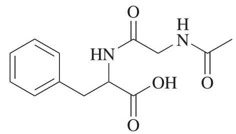
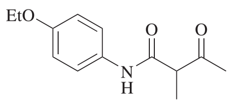
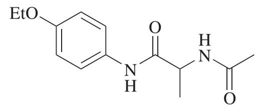
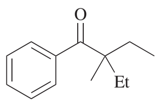
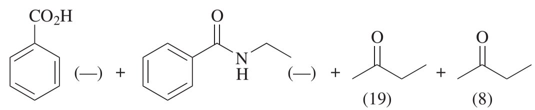
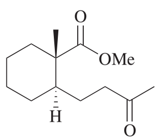
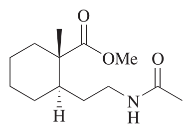
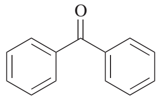
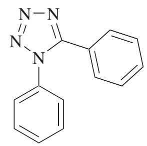
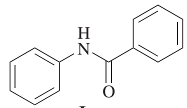
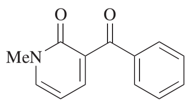
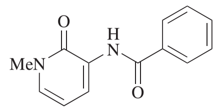
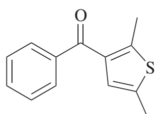
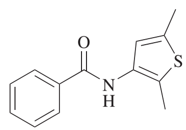
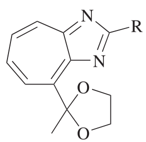
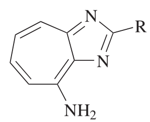
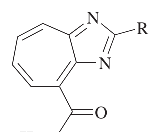
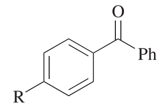
C_{12-18} 		NaN$_3$, H$_2$SO$_4$, 60°	 R: Cl (78); Br (64); O$_2$N (71); Ph (68)	325
C_{12-22} 		HN$_3$, H$_2$SO$_4$, CHCl$_3$, –5°, 45 min	 R^1, R^2: Me, Me (86); H, Ph (78); Ph, Ph (86)	326
C_{13} 		NaN$_3$, H$_2$SO$_4$, CHCl$_3$	 (20)	311
		NaN$_3$, H$_2$SO$_4$, CHCl$_3$	 (45)	311
		NaN$_3$, H$_2$SO$_4$, 0–40°, 3 h		327
		NaN$_3$, H$_2$SO$_4$, CHCl$_3$, 0°, 30 min	 (55)	328

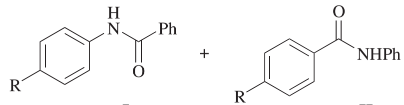
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	$SiCl_4$, NaN_3, MeCN, rt, 15 h	 (97)	70
	A. NaN_3, H_2SO_4, CCl_3CO_2H B. NaN_3, PPA, 50°, 8.5 h C. NaN_3, MsOH, DME, rt	 **I** Conditions: A (99); B (99); C (57)	1 54 56
	Azide, $FeCl_3$, DCE, rt	**I** Azide / Time: $TMSN_3$, 32 min (79); NaN_3, 2.5 h (70)	286
	NaN_3, H_2SO_4, $CHCl_3$, 0–50°, 12 h	 (70)	329
	NaN_3, CCl_3CO_2H, H_2SO_4, 50°, 3 h	 (58)	317
$C_{13–18}$ 	NaN_3, H_2SO_4, rt, 2 h	 **I** +  **II** R / I / II: Me (34) (0); Ph (84) (15)	330

C_{13-19}



NaN_3, CCl_3CO_2H, 60°, 8 h



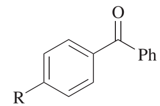
I + **II**

I + II (—)

R	**I:II**
Cl	3:2
O_2N	1:1
Me	1:1
MeO	3:2
Me_2N	1:1
Ph	1:1

7

C_{14}

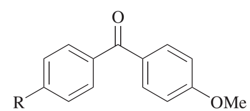


NaN_3, H_2SO_4, PhH, 50°, 8 h

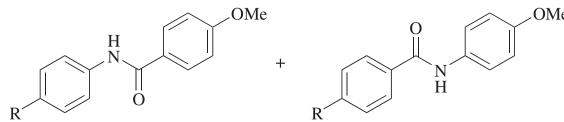
I + **II**

R	**I + II**	**I:II**
Me	(64)	1:1
MeO	(—)	2:1

331



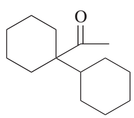
NaN_3, H_2SO_4, CCl_3CO_2H, 60°, 8 h



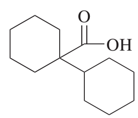
I + **II**

R	**I + II**	**I:II**
Cl	(97)	1:1
O_2N	(93)	1:1

6

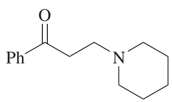


NaN_3, H_2SO_4, $CHCl_3$

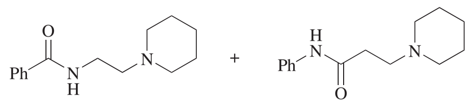


(75)

332



NaN_3, H_2SO_4

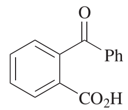
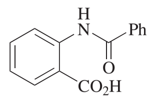
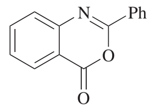
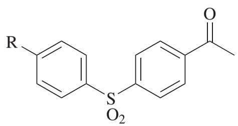
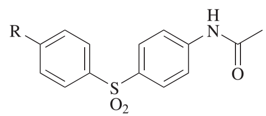
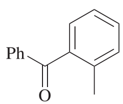
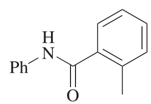
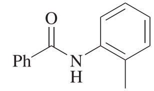
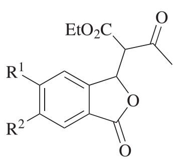
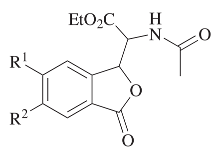


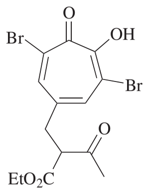
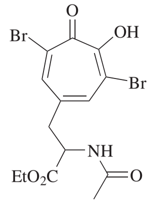
I + **II**

I + II (—), **I:II** = 1:1

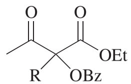
333

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

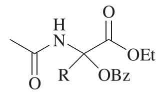
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	NaN_3, H_2SO_4, CCl_3CO_2H, 50°	 (91)	317
	NaN_3, H_2SO_4, $CHCl_3$	 (80)	334
	NaN_3, H_2SO_4	 (—) R: H, O_2N	248
	NaN_3, H_2SO_4, CCl_3CO_2H	 **I** +  **II**; **I** + **II** (97), **I**:**II** = 12:88	6
	NaN_3, H_2SO_4, CH_2Cl_2, PhH, 20°, 1 h	 R^1 / R^2: H / H (87); H / Cl (84); Cl / H (80); Cl / Cl (82)	319

	NaN_3, H_2SO_4, PhH, 0°, 1 h	 (97)		335

C_{14-17}

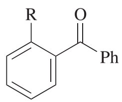


HN_3, H_2SO_4, CCl_4

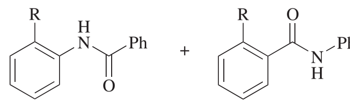


R	
Me	(58)
Et	(60)
n-Pr	(60)
n-Bu	(60)

336



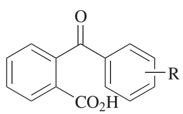
NaN_3, CCl_3CO_2H, 60°, 12 h



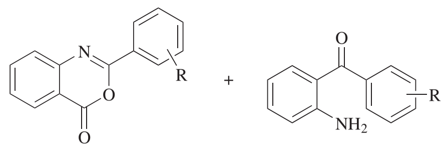
I + **II**

R	**I + II**	**I:II**
Me	(99)	24:76
HO_2C	(87)	100:0
Et	(96)	23:77
i-Pr	(96)	18:82

63



NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h

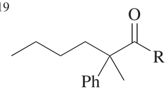
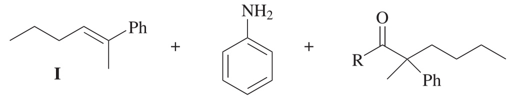
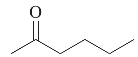
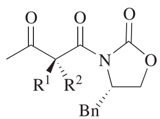
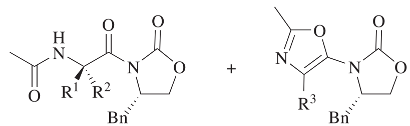
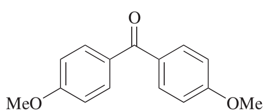
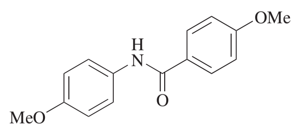


I + **II**

R	**I**	**II**
4-Cl	(84)	(3)
3-O_2N	(87)	(4)
4-MeO	(75)	(0)
2,4,6-Me_3	(29)	(0)

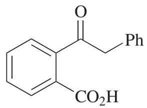
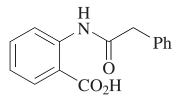
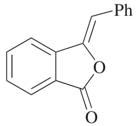
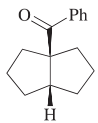
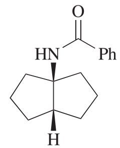
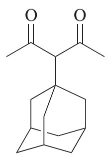
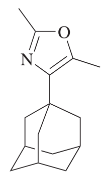
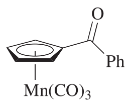
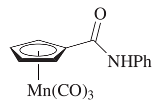
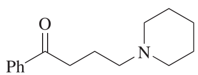
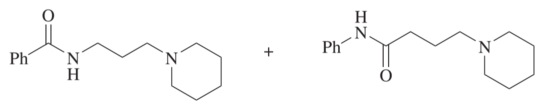
315

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{14–19}$ 	NaN_3, PPA, 50°, 8 h	 I + II + III +  IV	337
		R: Me — I (8), II (41), III (25), IV (29)	
		R: Ph — I (8), II (24), III (58), IV (—)	
$C_{14–23}$ 	A: NaN_3, MsOH, DME, –30° to rt B: NaN_3, H_2SO_4, DME, –30° C: NaN_3, H_2SO_4, PhH, 5° to rt	 I + II	56
C_{15} 	NaN_3, PPA, 50°, 8.5 h	 (91)	54

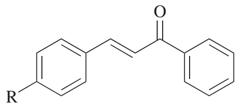
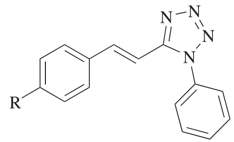
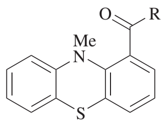
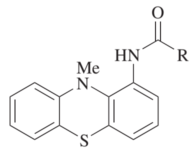
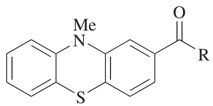
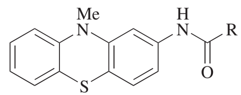
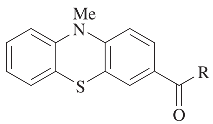
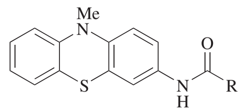
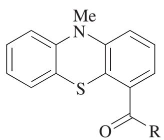
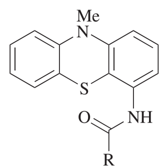
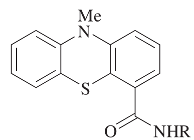
R	I	II	III	IV
Me	(8)	(41)	(25)	(29)
Ph	(8)	(24)	(58)	(—)

R^1	R^2	R^3	Conditions	I	II
H	H	H	A	(0)	(45)
H	Me	Me	A	(0)	(91)
Me	H	Me	C	(14)	(21)
H	Bn	Bn	A	(0)	(27)
H	Bn	—	B	(50)	(0)
H	Bn	—	C	(0)	(0)
$Ph(CH_2)_2$	H	$Ph(CH_2)_2$	A	(0)	(66)
H	(*E*)-PhCH=CHCH$_2$	(*E*)-PhCH=CHCH$_2$	A	(0)	(32)

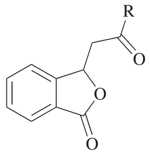
	NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h	 **I** (85)	315
	NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h	**I** (62)	315
	NaN_3, H_2SO_4, $CHCl_3$, 0°, 45 min	 (56)	338
	NaN_3, MsOH, DME, –30° to rt, 3 h	 (87)	56
	NaN_3, Promoter	 Promoter / Conditions: PPA, 65°, 19 h (67); H_2SO_4, — (15); TFA, — (32)	308
	NaN_3, H_2SO_4	 **I** + **II** (—), **I**:**II** = 3:7	333

Promoter	Conditions	
PPA	65°, 19 h	(67)
H_2SO_4	—	(15)
TFA	—	(32)

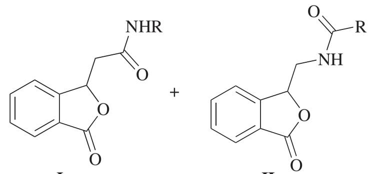
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15-16}			
	NaN_3, $SiCl_4$, MeCN, rt, 12 h	 R: H (94); Cl (95); MeO (90)	70
C_{15-20}			
	NaN_3, H_2SO_4, PhH, 0°	 R: Me (83); Ph (16)	339
	NaN_3, H_2SO_4, PhH, 0°	 R: Me (67); Ph (53)	339
	NaN_3, H_2SO_4, PhH, 0°	 R: Me (31); Ph (63)	339
	NaN_3, H_2SO_4, PhH, 0°	 **I** +  **II** R / I / II: Me (72) (0); Ph (34) (24)	339

C_{16}



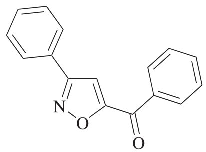
NaN_3, PPA, 20–90°, 4 h



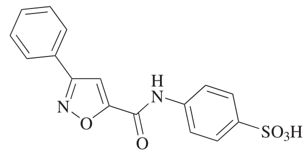
I + II

R	I	II
2-$O_2NC_6H_4$	(56)	(0)
4-$O_2NC_6H_4$	(92)	(—)

319

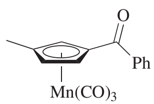


NaN_3, H_2SO_4, $CHCl_3$

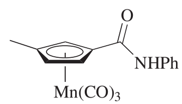


(100)

340



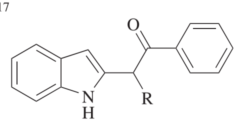
NaN_3, Promoter



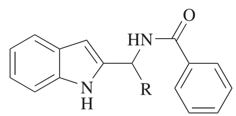
Promoter	Conditions	
PPA	65°, 19 h	(53)
H_2SO_4	—	(26)
TFA	—	(20)

308

C_{16-17}



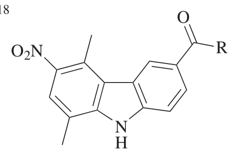
NaN_3, H_2SO_4, $CHCl_3$, rt



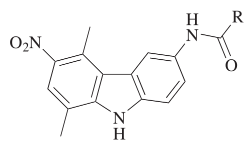
R	
H	(38)
Me	(56)

341

C_{16-18}



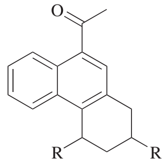
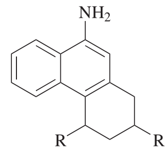
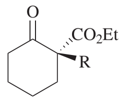
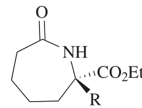
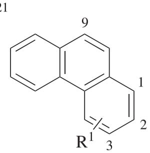
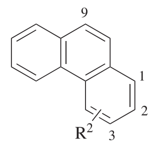
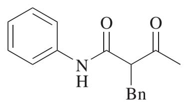
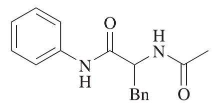
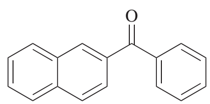
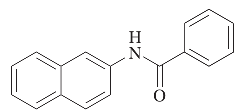
NaN_3, TFA, 100°, 5 h



R	
Me	(71)
Et	(70)
n-Pr	(72)

342

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16-18} 	1. NaN_3, H_2SO_4, 60°, 8 h 2. Hydrolysis	 R: H (81); Me (82)	5
C_{16-20} 	NaN_3, MsOH, $CHCl_3$, reflux, 1 h	 R: Bn (97); 2-$C_{10}H_7CH_2$ (71)	108
C_{16-21} 	1. NaN_3, H_2SO_4, 60°, 8 h 2. Hydrolysis	 R^1 / R^2: 2-Ac / 2-H_2N (88); 3-Ac / 3-H_2N (80); 9-Ac / 9-H_2N (73); 1-Bz / 1-BzHN (93)	5
C_{17} 	NaN_3, H_2SO_4, $CHCl_3$	 (40)	311
	NaN_3, PPA, 50°, 10 h	 (72)	54

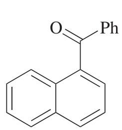
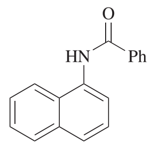
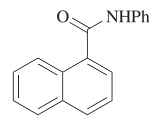
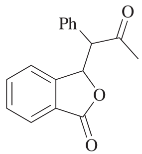
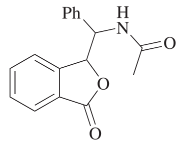
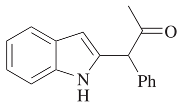
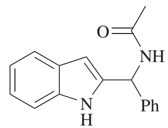
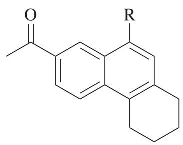
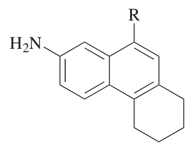
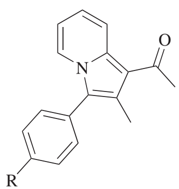
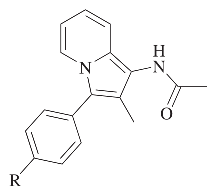
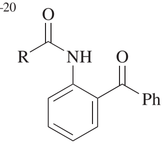
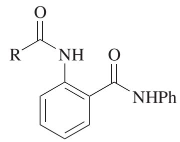
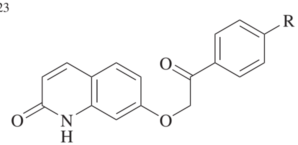
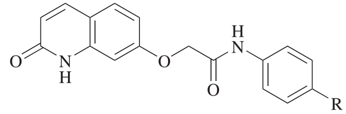
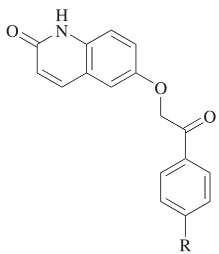
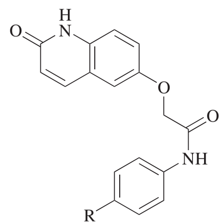
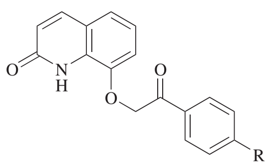
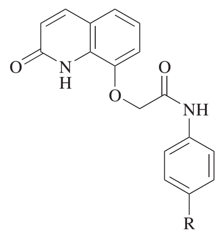
	NaN_3, CCl_3CO_2H, 60°, 12 h	 (29) +  (69)	63
	NaN_3, PPA, 0° to rt, 3 h	 (95)	343
	NaN_3, H_2SO_4, $CHCl_3$, rt	 (40)	341
C_{17-18}			
	1. NaN_3, H_2SO_4, 60°, 8 h 2. Hydrolysis	 R: Me (93); Et (99)	5
	HN_3, H_2SO_4, $CHCl_3$, 0°, 30 min	 R: H (64); Cl (77); O_2N (56); MeO (71)	344

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17-20} 	NaN_3, H_2SO_4, $CHCl_3$, rt, 12 h	 (—) R: *n*-Pr; Ph; 2-$O_2NC_6H_4$	345
C_{17-23} 	NaN_3, H_2SO_4, rt, 10 min	 R: H (94); F (92); MeO (80); Ph (98)	346
	NaN_3, H_2SO_4, rt, 10 min	 R: H (85); F (73); MeO (93); Ph (95)	346
	NaN_3, H_2SO_4, rt, 10 min	 R: H (96); F (92); MeO (96); Ph (75)	346

C_{18}

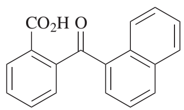
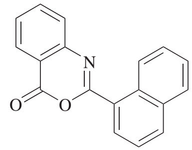
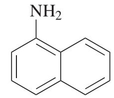
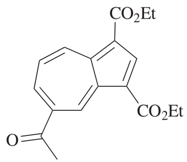
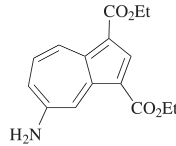
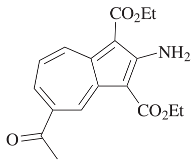
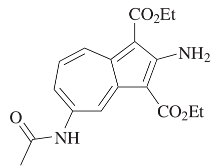
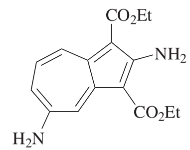
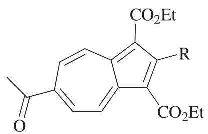
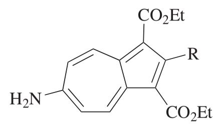
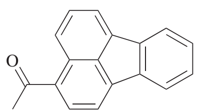
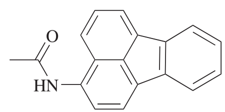
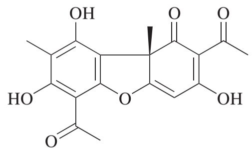
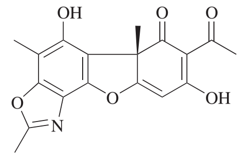
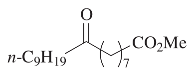
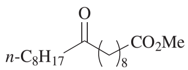
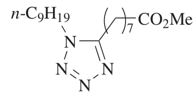
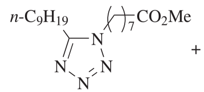
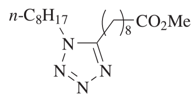
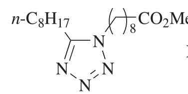
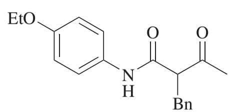
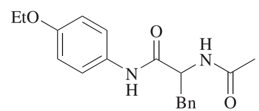
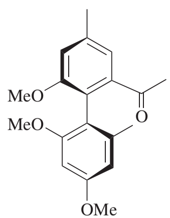
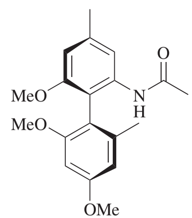
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h	 (51) +  (7)	315
	NaN_3, H_2SO_4, $CHCl_3$, rt, 12 h	 (—)	347
	NaN_3, H_2SO_4, $CHCl_3$, rt, 12 h	 (—) +  (—)	347
	NaN_3, H_2SO_4, $CHCl_3$, rt, 12 h	 (—) R: H, H_2N	347
	NaN_3, TFA, 60°, 6 h	 (50)	348

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	NaN_3, $CHCl_3$, 50–60°, 2 h	 (70)	349
C_{19}  + 	NaN_3, $TiCl_4$, MeCN, reflux, 5 h	 **I** +  **II** +  **III** +  **IV** **I** + **II** + **III** + **IV** (71)	350
	NaN_3, H_2SO_4, $CHCl_3$	 (53)	311
	NaN_3, TFA, 60°, 27 h	 (43)	351

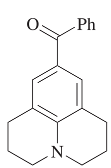
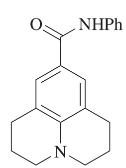
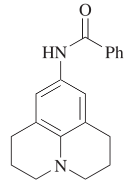
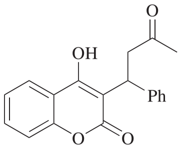
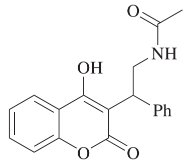
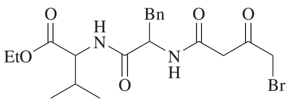
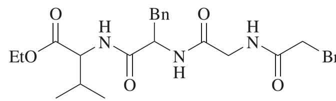
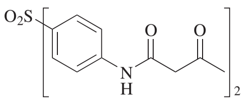
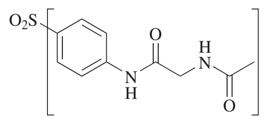
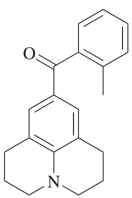
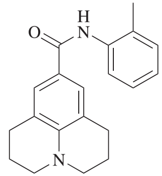
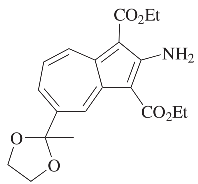
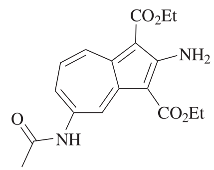
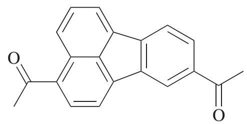
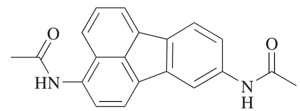
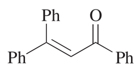
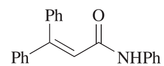
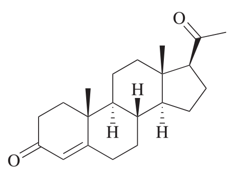
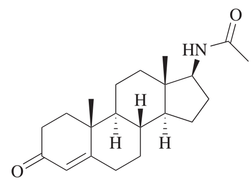
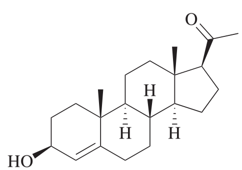
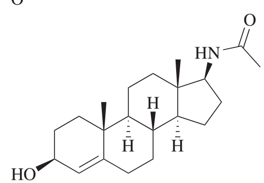
		NaN_3, H_2SO_4, CCl_3CO_2H, 60°, 3 h	 (—) +  (—)	273
		NaN_3, H_2SO_4, $CHCl_3$, rt, 2 h	 (90)	352
C_{20}		HN_3, H_2SO_4	 (31)	291
		NaN_3, H_2SO_4, $CHCl_3$	 (40)	311
		NaN_3, H_2SO_4, PhH, rt	 (76)	273

TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	NaN_3, H_2SO_4, $CHCl_3$, rt, 12 h	 (—)	347
	NaN_3, TFA, 60°, 6 h	 (99)	348
C_{21}			
	NaN_3, H_2SO_4, $CHCl_3$, 35°, 1 h	 (40)	353
	NaN_3 (1 eq), PPA, 50°, 10 h	 (35)	354
	HN_3, H_2SO_4, $CHCl_3$, rt, 30 min	 (82)	355

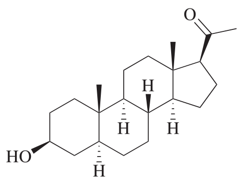
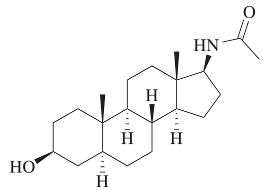
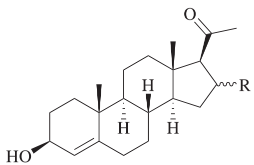
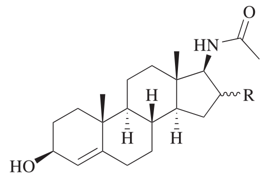
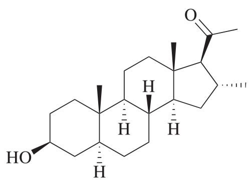
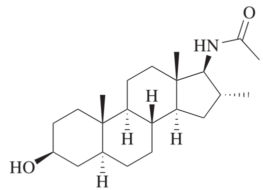
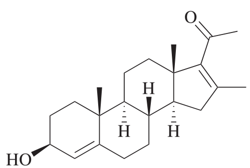
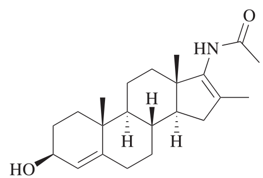
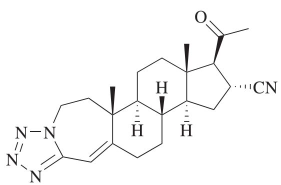
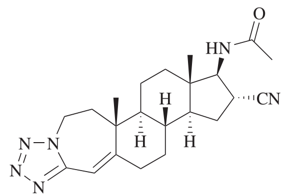
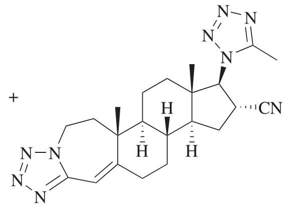
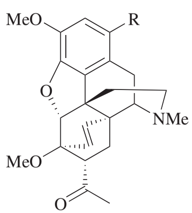
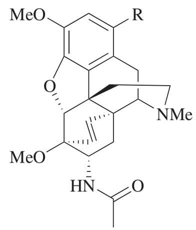
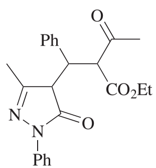
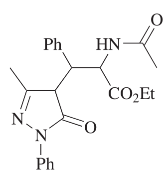
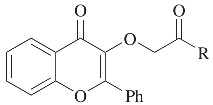
C_{22}				
	HN_3, H_2SO_4, $CHCl_3$, rt, 30 min		(80)	355
	HN_3, H_2SO_4, $CHCl_3$, rt, 30 min		R: α-Me (88); β-Me (82)	355
	HN_3, H_2SO_4, $CHCl_3$, rt, 30 min		(85)	355
	HN_3, H_2SO_4, $CHCl_3$, rt, 30 min		(65)	355

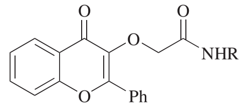
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}			
	HN_3, BF_3•OEt_2, $CHCl_3$, 0° to rt, 24 h	 (25) +  (20)	356
C_{23}			
	A. NaN_3, perchloric acid, 75°, 5 h B. NaN_3, HCl (concd), 60°, 6 h	 R / Conditions H / A / (50) Cl / B / (23)	357
	NaN_3, H_2SO_4, $CHCl_3$, 0–50°, 5 h	 (48)	263

C_{23-29}

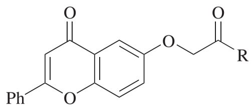


NaN$_3$, H$_2$SO$_4$, rt, 1 h

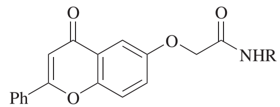


R	
Ph	(78)
4-FC$_6$H$_4$	(85)
4-MeOC$_6$H$_4$	(72)
2-C$_{10}$H$_7$	(71)
4-PhC$_6$H$_4$	(65)

358

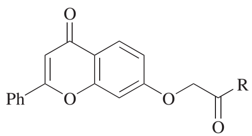


NaN$_3$, H$_2$SO$_4$, rt, 1 h

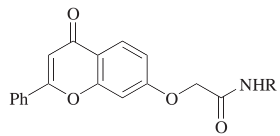


R	
Ph	(91)
4-FC$_6$H$_4$	(96)
4-MeOC$_6$H$_4$	(94)
2-C$_{10}$H$_7$	(89)
4-PhC$_6$H$_4$	(61)

358



NaN$_3$, H$_2$SO$_4$, rt, 1 h



R	
Ph	(87)
4-FC$_6$H$_4$	(85)
4-MeOC$_6$H$_4$	(67)
2-C$_{10}$H$_7$	(77)
4-PhC$_6$H$_4$	(85)

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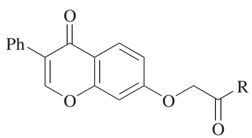
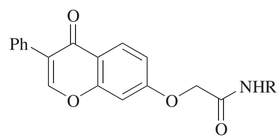


NaN$_3$, H$_2$SO$_4$, rt, 1 h



R	
Ph	(89)
4-FC$_6$H$_4$	(93)
4-MeOC$_6$H$_4$	(91)
2-C$_{10}$H$_7$	(88)
4-PhC$_6$H$_4$	(90)

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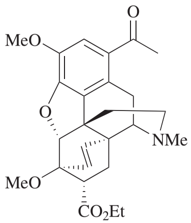
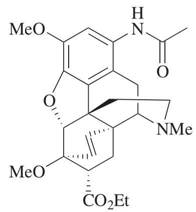
TABLE 3. SCHMIDT REACTIONS OF ACYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26}			
	NaN_3, HCl (concd), rt, 12 h	 (35)	359

[a] Silica sulfuric acid is silica-bound sulfuric acid generated by treating silica gel with chlorosulfonic acid.

[b] The reaction was performed in the presence of 1 equivalent of dimethyl phosphite.

[c] The reaction was performed in the presence of 1 equivalent of diethyl phosphite.

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3

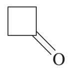
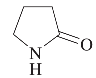
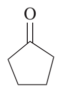
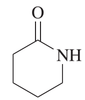
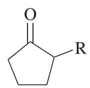
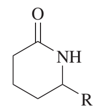
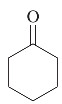
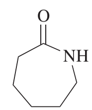
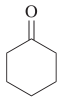
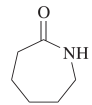
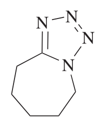
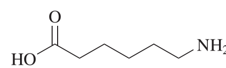
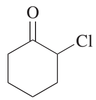
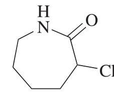
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	HN_3, H_2SO_4, $CHCl_3$, rt, 2 h	 (20)	360
C_5 	NaN_3, silica sulfuric acid,[a] 60°, 25 min	 (95)	282
C_{5-8} 	HN_3, H_2SO_4, $CHCl_3$, 5°, 1 h	 **I** R: H (80), Me (75), Et (63), *n*-Pr (61), *i*-Pr (46)	53
	NaN_3, PPA, 50°, 9–14 h	**I** R: H (83), Me (87), *n*-Pr (82)	54
C_6 	NaN_3, HCl	 (63) **I**	1
	NaN_3, AcOH, HBr (cat)	**I** (56)	1

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

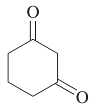
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$TMSN_3$, Promoter (x eq), DCE, rt	 **I** Promoter / *x* / Time (h) $FeCl_3$ 1.0 0.5 (82) $FeCl_3$ 0.1 12 (78) $InBr_3$ 0.5 3 (40) $InCl_3$ 0.5 3 (30) $ZrCl_4$ 0.5 3 (15)	286
	NaN_3, $FeCl_3$ (1 eq), DCE, rt, 3 h	**I** (70)	286
	NaN_3, MsOH, DME, –30° to rt, 3 h	**I** (96)	56
	NaN_3, PPA, 50°, 8 h	**I** (89)	54
	NaN_3, silica sulfuric acid,[a] 60°, 35 min	**I** (92)	282
	NaN_3, P_2O_5–SiO_2, MW, 7 min	**I** (70)	289
	NaN_3, $Fe(HSO_4)_3$, grinding, 50°, 20 min	**I** (88)	288
	NaN_3, $SiCl_4$, MeCN, rt, 20 h	 (95)	70
	1. NaN_3, H_2SO_4 2. HCl	 (90)	195



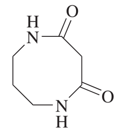
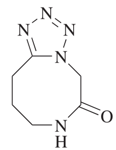
HN$_3$, H$_2$SO$_4$, CHCl$_3$, 40–45°, 1 h

 (31)

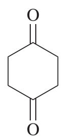
53



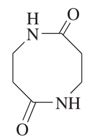
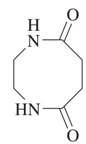
HN$_3$, H$_2$SO$_4$, CHCl$_3$, rt, 24 h

 (—) +  (—)

361



HN$_3$, HCl, CHCl$_3$

 + 

I + **II**

I + II (20–27)

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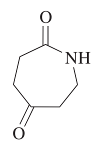
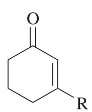
Azide, FeCl$_3$, DCE, rt



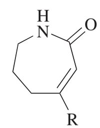
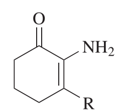
Azide	Time	
TMSN$_3$	55 min	(68)
NaN$_3$	3.5 h	(68)

286

C$_{6–7}$



NaN$_3$, PPA, 40°, 6 h

 + 

I + **II**

R	**I**	**II**
H	(13)	(—)
Me	(—)	(—)

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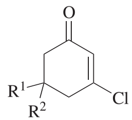
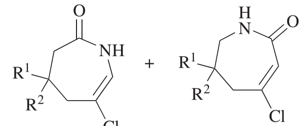
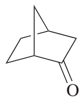
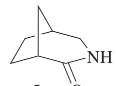
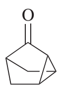
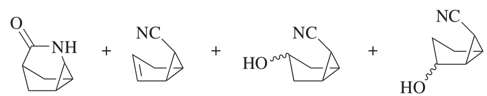
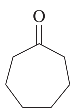
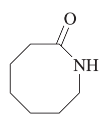
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{6–8}$ 	NaN_3, PPA, 120°, 2 h	 **I** + **II** R^1 / R^2 / **I** / **II** H / H / (11) / (15) Me / H / (17) / (35) Me / Me / (32) / (36)	364 365 365
C_7 	NaN_3, H_2SO_4, PhH, 15°	 **I** (10)	366
	HN_3, H_2SO_4, P_2O_5, $CHCl_3$, 0° to rt, 4 h	**I** (43)	367
	NaN_3, HCl, 5°, 5 h	**I** (16)	367
	NaN_3, PPA, 60°, 2 d	**I** (34)	368
	NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 12 h	 **I** + **II** + **III** + **IV** **I** (11), **II** (13), **III** + **IV** (33)	369
	NaN_3, PPA, 50°, 9 h	 **I** (89)	54
	NaN_3, silica sulfuric acid,[a] 60°, 35 min	**I** (92)	282

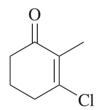
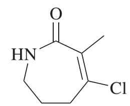
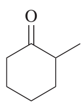
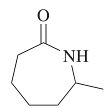
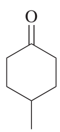
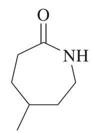
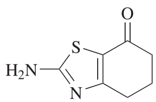
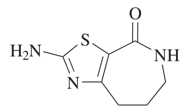
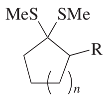
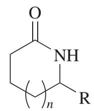
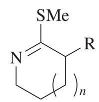
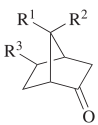
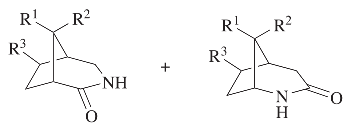
	NaN_3, P_2O_5–SiO_2, MW, 7 min	**I** (72)	289
	NaN_3, $Fe(HSO_4)_3$, grinding, 50°	**I** (90)	288
	Azide, $FeCl_3$, DCE, rt	**I** Azide / Time $TMSN_3$ / 45 min (80) NaN_3 / 3 h (72)	286
	NaN_3, PPA, 120°, 2 h	 (54)	370
	NaN_3, silica sulfuric acid,[a] 60°, 30 min	 (95) **I**	282
	NaN_3, P_2O_5–SiO_2, MW, 7 min	**I** (75)	289
	NaN_3, silica sulfuric acid,[a] 60°, 25 min	 (95) **I**	282
	NaN_3, P_2O_5–SiO_2, MW, 7 min	**I** (70)	289
	NaN_3, $Fe(HSO_4)_3$, grinding, 50°, 20 min	**I** (90)	288

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	NaN_3, H_2SO_4, $CHCl_3$, rt, 24 h	 (88)	371
C_{7-10}			
	1. IN_3, CH_2Cl_2, –78 to –10°, 2 h 2. TFA, $CHCl_3$, rt, 2 h	 *n* / R 1 / H (73) 2 / H (76) 2 / Me (60) 3 / H (59) 4 / H (65)	83
	$TMSN_3$, $SnCl_4$, I_2, CH_2Cl_2, –78° to rt, 2.5 h	 *n* / R 1 / H (95) 2 / H (46) 2 / Me (31) 3 / H (51) 4 / H (38)	83
C_{7-14}			
	NaN_3, H_2SO_4, $CHCl_3$, rt, 1–36 h	 **I** + **II**	68

R^1	R^2	R^3	**I + II**	**I:II**
H	H	H	(35)	100:0
H	MeO	H	(48)	73:27
H	Cl	H	(28)	85:15
H	Br	H	(37)	81:19
H	TsO	H	(52)	35:65

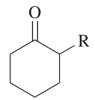
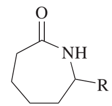
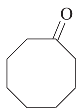
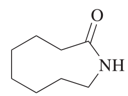
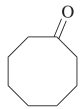
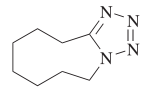
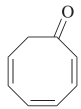
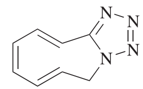
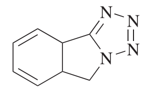
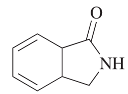
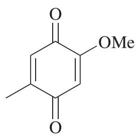
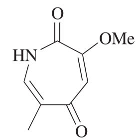
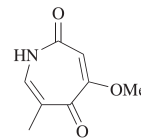
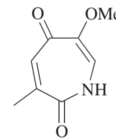
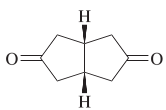
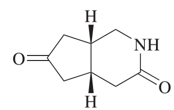
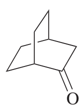
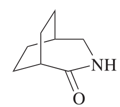
Substrate	Conditions	Product(s) and Yield(s) (%)					Refs.
		Cl	H	H	(29)	83:17	
		Br	H	H	(41)	100:0	
		TsO	H	H	(40)	36:64	
		MeO_2C	H	H	(31)	66:34	
		MeO_2C	H	Br	(52)	52:48	
C_{7-18} 	NaN_3, H_2SO_4 or PPA, 0–50°, 1–10 h		R				
			Me	(96)			54
			NC–	(76)			54
			Et	(93)			53
			n-Pr	(97)			53
			EtO_2C	(80)			53
			i-Bu	(77)			372
			n-C_6H_{13}	(16)			372
			Bn	(49)			368
			4-$MeC_6H_4CH_2$	(45)			368
			2-$MeOC_6H_4CH_2$	(42)			368
			4-$MeOC_6H_4CH_2$	(40)			368
			n-$C_{12}H_{25}$	(25)			372
C_8 	NaN_3, silica sulfuric acid,[a] 60°, 25 min	 **I**	(92)				282
	NaN_3, P_2O_5–SiO_2, MW, 7 min	**I** (70)					289
	NaN_3, $Fe(HSO_4)_3$, grinding, 50°, 25 min	**I** (92)					288

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	NaN_3, H_2SO_4, 0° to rt, 12 h	 (—)	373
	NaN_3, TFA, 0° to rt, 6 h	 (—) +  (—)	373
	NaN_3, HCl, 0° to rt, 5 h	 (66)	373
	NaN_3, H_2SO_4, 0–70°, 70 h	 (22) +  (16) +  (13)	374
	NaN_3, HCl, rt, 3 h	 (52)	116
	HN_3, AcOH, 0° to rt, 3 h	 (56)	375

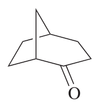
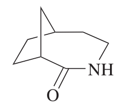
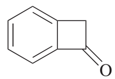
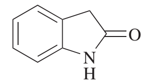
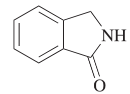
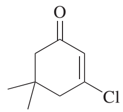
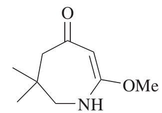
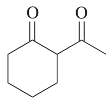
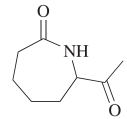
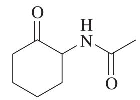
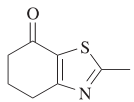
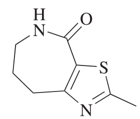
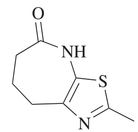
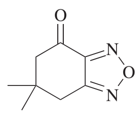
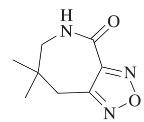
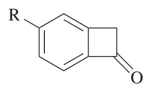
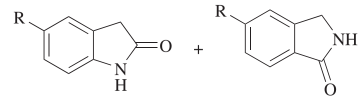
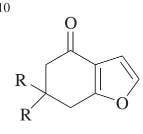
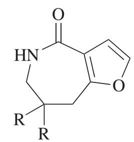
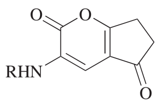
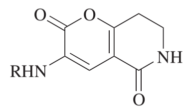
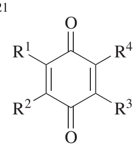
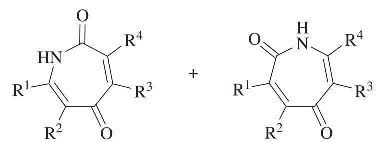
	HN_3, H_2SO_4, P_2O_5, $CHCl_3$, 0° to rt, 20 h	 (40)	376
	NaN_3, CCl_3CO_2H,[b] 65°	 **I** +  **II** **I** + **II** (—), **I**:**II** = 1:9	59
	NaN_3, PPA, MeOH, reflux, 4 h	 (36)	377
	NaN_3, PPA, 40°, 6 h	 (32) +  (6)	378
	NaN_3, H_2SO_4, 0°, 10 h	 (68) +  (—)	55
	NaN_3, H_2SO_4, $CHCl_3$, rt, 24 h	 (55)	371

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 	NaN_3, H_2SO_4, PhH, 60°	 **I** + **II**	
		R | **I + II** | **I:II**	
		H | (—) | 7:3	59
		MeO | (—) | 1:9	
C_{8-10} 	NaN_3, H_2SO_4, 0°, 10 h		379
		R	
		H (79)	
		Me (79)	
C_{8-15} 	$TMSN_3$, H_2SO_4, CH_2Cl_2, rt, 3 h		380
		R	
		H (67)	
		Bz (71)	
C_{8-21} 	NaN_3, H_2SO_4	 **I** + **II** (—)	

R^1	R^2	R^3	R^4	**I**	Refs.
H	Me	H	Me	(80)	71
H	Me	Me	Me	(80)	71
H	*i*-Pr	H	Me	(75)	71
Me	Me	Me	Me	(80)	71
H	Me	H	*i*-Pr	(—)	381
H	H	Bn	Bn	(—)	381
Me	H	Bn	Bn	(—)	381

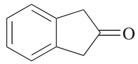
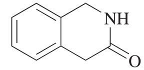
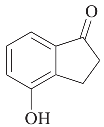
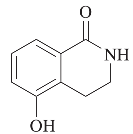
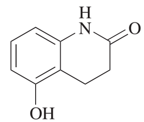
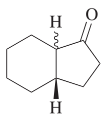
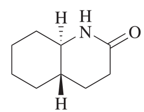
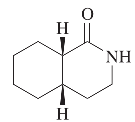
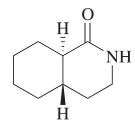
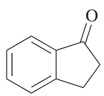
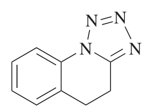
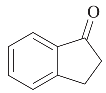
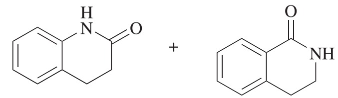
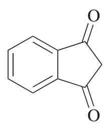
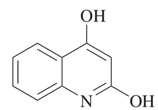
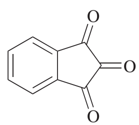
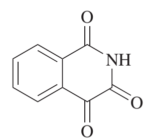
C_9 	NaN_3, H_2SO_4, $CHCl_3$, 40°, 3 h	 (87)	382
	NaN_3, TFA, 70°, 18 h	 **I** (76)	383
	$TMSN_3$, MsOH, MsCl, <5°	**I** +  **II** — **I + II** (92), **I**:**II** = 1:2.5	384
	NaN_3, H_2SO_4, $CHCl_3$, rt, 1 h	 **I** +  **II** +  **III** — **I + II + III** (—), **I**:**II**:**III** = 3.5:2.6:1	385
	NaN_3, $SiCl_4$, MeCN, rt, 13 h	 (93)	70

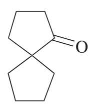
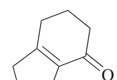
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	NaN_3, H_2SO_4	 **I** + **II**	386

Solvent	Temp	Time	**I** + **II**	**I**:**II**
Et_2O	rt	4 h	(0)	—
Et_2O	reflux	1 h	(0)	—
Et_2O	reflux	4 h	(0)	—
PhH	60°	4 h	(100)	68:32
PhH	60°	10 min	(100)	71:29
PhH	rt	4 h	(100)	68:32

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3, PPA, 50°, 10 h	**I** (90)	54
	NaN_3, PPA, 50–60°	**I** + **II** (60), **I**:**II** = 76:24	387
	NaN_3, H_2SO_4, $CHCl_3$, 0–30°, 3 h	 (—)	388
	Azide, $FeCl_3$, DCE, rt		286

Azide	Time	
$TMSN_3$	40 min	(82)
NaN_3	3 h	(72)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3, PPA, 60°, 7 h	 (33)	389

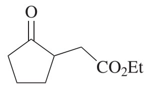
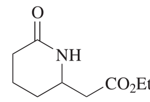
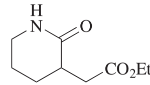
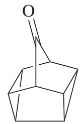
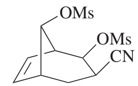
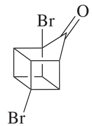
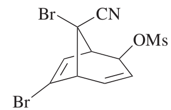
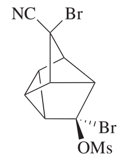
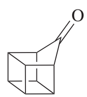
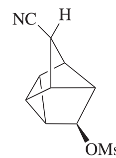
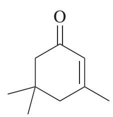
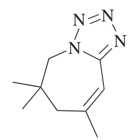
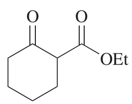
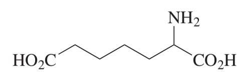
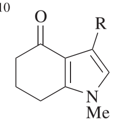
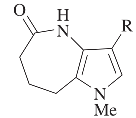
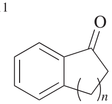
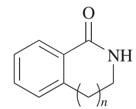
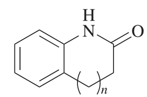
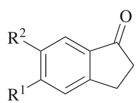
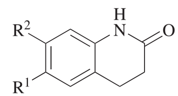
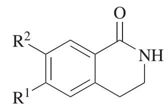
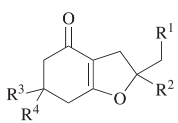
	1. HN_3, HCl (g), $CHCl_3$, 5°, 3 h 2. HCl (concd), reflux, 3 h	 **I** +  **II** **I + II** (50)	284
	NaN_3, MsOH, CH_2Cl_2, 0°, 20 min	 (20)	390
	NaN_3, MsOH, CH_2Cl_2, 0°, 10 min	 (62) +  (12)	81
	NaN_3, MsOH, CH_2Cl_2, 0°, 10 min	 (60)	391
	NaN_3, $SiCl_4$, MeCN, rt, 5 h	 (95)	70
	NaN_3, HCl, H_2O	 (20)	1

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

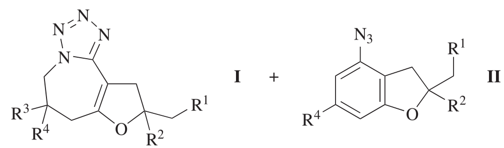
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10} 	NaN_3, H_2SO_4, $CHCl_3$, rt, 30 min	 R: H (40); Me (31)	392
C_{9-11} 	NaN_3, HCl (concd)	 **I** +  **II** n = 1: I (—), II (—) n = 2: I (—), II (—) n = 3: I (7), II (87)	393
	A: NaN_3, H_2SO_4, PhH, 60° B: NaN_3, CCl_3CO_2H,[b] 65°	 **I** +  **II** **I** + **II** (—)	59

R^1	R^2	Conditions	I:II
H	H	A	7:3
H	H	B	1:4
H	HO	A	1:4
H	HO	B	1:9
HO	H	A	9:1
HO	H	B	1:4
H_2N	H	A	1:1
H_2N	H	B	1:9
H	H_2N	A	9:1
H	H_2N	B	1:4
Cl	H	A	3:2
Cl	H	B	1:9
H	Cl	A	4:1

H	Cl	B	1:9
O_2N	H	A	9:1
O_2N	H	B	1:9
H	O_2N	A	4:1
H	O_2N	B	1:4
MeO	H	A	1:9
MeO	H	B	1:9
H	MeO	A	7:3
H	MeO	B	1:4
AcHN	H	A	9:1
AcHN	H	B	1:9
H	AcHN	A	9:1
H	AcHN	B	—
AcO	H	A	—
AcO	H	B	1:4
H	AcO	A	—
H	AcO	B	1:9



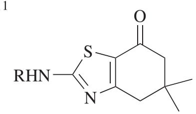
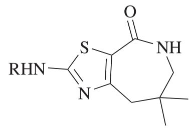
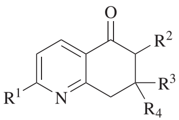
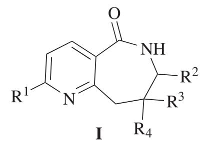
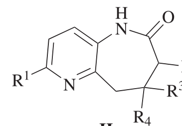
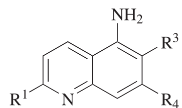
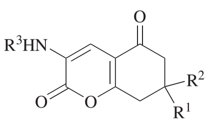
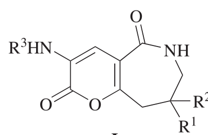
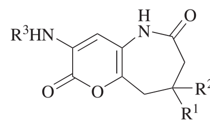
NaN_3, $SiCl_4$, MeCN, rt



394

R^1	R^2	R^3	R^4	**I**	**II**
Br	H	H	H	(68)	(—)
Br	H	Me	H	(56)	(—)
Br	Me	H	H	(89)	(—)
Br	H	Me	Me	(65)	(—)
I	H	H	H	(42)	(18)
I	H	H	Me	(44)	(14)
I	Me	H	H	(42)	(19)
I	H	Me	Me	(50)	(—)

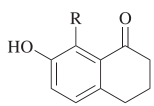
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-11} 	NaN_3, H_2SO_4, $CHCl_3$, rt, 24 h	 R: H (—); Ac (—)	371
C_{9-15} 	NaN_3, H_2SO_4	 **I** +  **II** +  **III**	395
C_{9-18} 	A: NaN_3, H_2SO_4, $CHCl_3$, –15 to 0°, 5 h B: NaN_3, H_2SO_4, $CHCl_3$, rt, 2 h C: TMSN$_3$, H_2SO_4, CH_2Cl_2, 35°, 2 h D: TMSN$_3$, H_2SO_4, CH_2Cl_2, –15 to 0°, 5 h	 **I** +  **II**	380

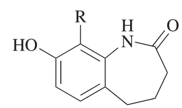
R^1	R^2	R^3	R^4	I	II	III
H	H	H	H	(16)	(11)	(36)
Me	H	H	H	(7)	(17)	(33)
MeO	H	H	H	(12)	(46)	(15)
H	H	H	H_2NCO	(19)	(0)	(0)
H	H	Me	Me	(6)	(12)	(57)
H	Ph	H	H	(0)	(0)	(0)

R^1	R^2	R^3	Conditions	**I + II**	**I:II**
H	H	H	A	(78)	10:1
H	H	H	B	(85)	3.3:1
H	H	H	C	(81)	4.5:1
H	Me	H	A	(94)	38:1
H	Me	H	B	(96)	3.2:1
H	Me	H	C	(99)	4.2:1
H	Me	H	D	(96)	20:1
Me	Me	H	A	(85)	17.5:1
Me	Me	H	C	(83)	2.3:1
H	H	Bz	B	(99)	3.9:1
H	H	Bz	D	(98)	21:1
H	Me	Bz	B	(97)	4.3:1
H	Me	Bz	D	(92)	10:1
Me	Me	Bz	A	(99)	9:1
Me	Me	Bz	B	(98)	3.1:1
Me	Me	Bz	D	(98)	18:1

C_{10}

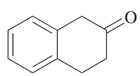


NaN_3, MsOH, 8°, 1 h

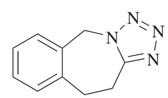


R	
H	(76)
O_2N	(84)

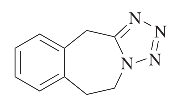
287



HN_3, BF_3•OEt_2, PhH, rt, 24 h



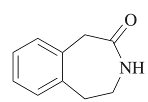
(21) +



(9)

396

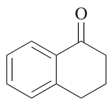
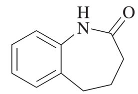
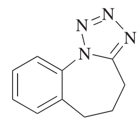
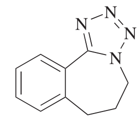
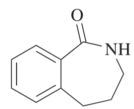
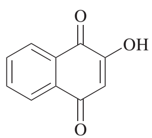
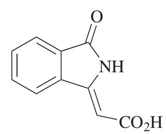
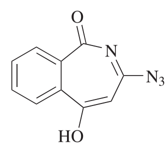
Azide, $FeCl_3$, DCE, rt



Azide	Time	
$TMSN_3$	46 min	(70)
NaN_3	2.5 h	(67)

286

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	NaN_3, CCl_3CO_2H,[b] 60°	 **I** (85)	1
	Azide, $FeCl_3$, DCE, rt	**I** — Azide / Time: $TMSN_3$, 40 min (80); NaN_3, 2.5 h (75)	286
	HN_3, BF_3•OEt_2, PhH, rt, 24 h	**I** (5) +  **II** (33) +  **III** (2)	396
	NaN_3, HCl, 0° to rt, 4 h	**I** (42) + **III** (23) +  (13)	397
	NaN_3 (1.3 eq), H_2SO_4, 5° to rt, 2 h	 (80)	398
	NaN_3 (10 eq), H_2SO_4, 0°, 15 min	 (69)	398

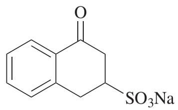
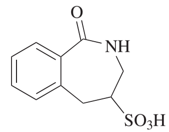
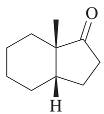
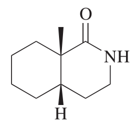
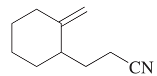
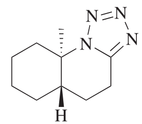
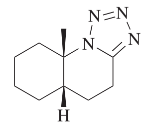
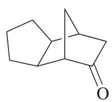
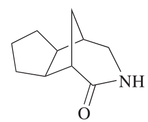
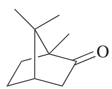
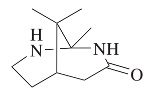
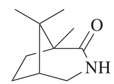
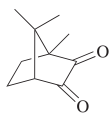
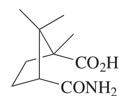
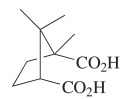
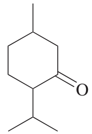
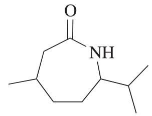
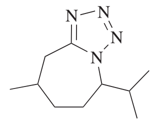
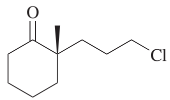
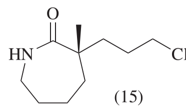
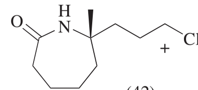
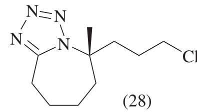
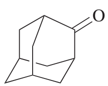
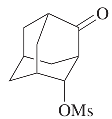
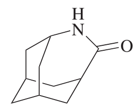
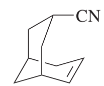
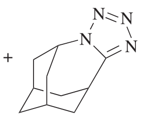
	HN_3	 (—)	399
	HN_3, H_2SO_4, PhH, 0°, 20 min	 (—) +  (—) +  (—) +  (—)	400
	NaN_3, H_2SO_4, 0°	 (—)	366
	NaN_3, H_2SO_4, $CHCl_3$, 30–50°, 7 h	 **I** (40) +  (5)	401
	NaN_3, H_2SO_4, $CHCl_3$	**I** (30)[c]	77
	NaN_3, H_2SO_4, $CHCl_3$, 0°, 3 h	 (57) +  (14)	402

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	NaN_3, H_2SO_4, rt, 50 h	 (70) +  (16)	55
	NaN_3, TFA, H_2O	 (15) +  (42) +  (28)	29
	NaN_3	 I +  II +  III +  IV	

Conditions	I	II	III	IV	Refs.
MsOH, rt, 50 h	(88)	(11)	(0)	(0)	403
MsOH, AcOH, rt, 50 h	(3)	(33)	(61)	(0)	403
TFA, rt, 3 h	(0)	(60)	(40)	(0)	403
MsOH, $CHCl_3$, rt, 20 h	(36)	(34)	(10)	(8)	403
MsOH, AcOH, 24 h	(0)	(70)	(30)	(0)	403
AcOH, *p*-TsOH	(0)	(31)	(0)	(0)	404

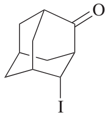
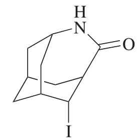
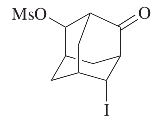
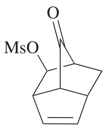
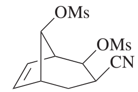
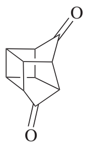
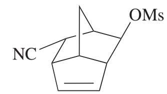
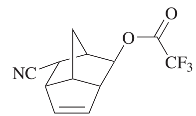
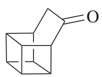
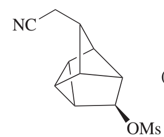
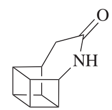
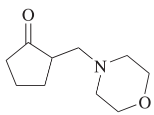
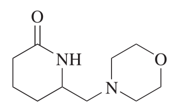
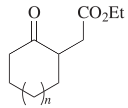
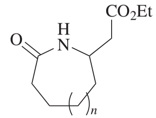
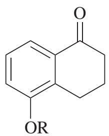
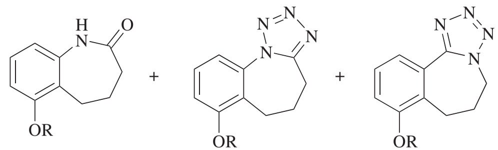
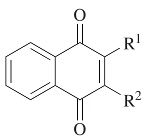
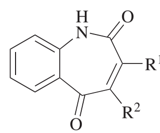
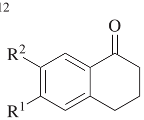
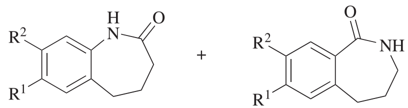
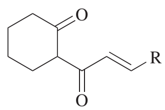
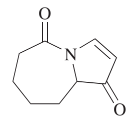
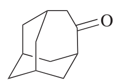
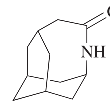
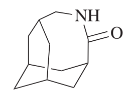
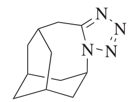
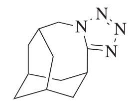
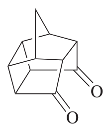
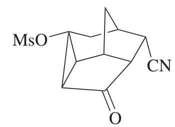
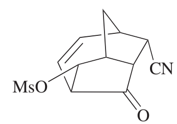
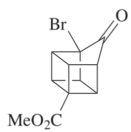
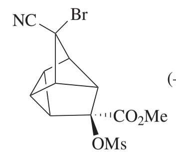
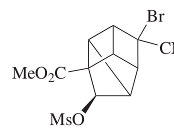
	NaN_3, MsOH, rt, 1 h	 (15) +  (6)	405
	NaN_3, MsOH	 (40)	390
	NaN_3, MsOH, 0°, 1 h	 (45)	406
	NaN_3, TFA, 0°, 1 h	 (—)	406
	NaN_3, MsOH, CH_2Cl_2, 0°, 15 min	 (60) +  (32)	407
	NaN_3, H_2SO_4, 0° to rt, 5 h	 (20)	408

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-11}			
	NaN_3, H_2SO_4, 0°, 10 h	 n: 1 (74); 2 (80)	409
	NaN_3, CCl_3CO_2H,[b] reflux, 6 h	 I + II + III R / I / II + III: H (59) (11); Me (55) (6)	410
	NaN_3, H_2SO_4, rt	 R^1 / R^2: H Cl (22); Cl Cl (49); Cl Br (12); H Me (50)	411
C_{10-12}			
	A: NaN_3, H_2SO_4, PhH, 60° B: NaN_3, CCl_3CO_2H,[b] 65°	 I + II I + II (—)	59

R^1	R^2	Conditions	**I**:**II**
H	H	A	4:1
H	H	B	7:3
H_2N	H	A	4:1
H_2N	H	B	4:1
H	H_2N	A	9:1
H	H_2N	B	3:2
HO	H	A	3:2
HO	H	B	2:3
H	HO	A	4:1
H	HO	B	7:3
Cl	H	A	9:1
Cl	H	B	3:2
H	Cl	A	4:1
H	Cl	B	7:3
O_2N	H	A	9:1
O_2N	H	B	4:1
H	O_2N	A	9:1
H	O_2N	B	9:1
MeO	H	A	1:1
MeO	H	B	1:1
H	MeO	A	4:1
H	MeO	B	7:3
AcHN	H	A	9:1
AcHN	H	B	2:3
H	AcHN	A	9:1
H	AcHN	B	7:3
AcO	H	A	—
AcO	H	B	7:3
H	AcO	A	—
H	AcO	B	7:3

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-16}			
	NaN_3 (2 eq), H_2SO_4	 + RNH_2 (—) R: Me (76); Ph (76); 4-$O_2NC_6H_4$ (82); 4-$MeOC_6H_4$ (70)	412
C_{11}			
	NaN_3, MsOH, rt, 24 h	 **I** +  **II** +  **III** +  **IV** **I** + **II** (7), **I**:**II** = 1:1 **III** + **IV** (48), **III**:**IV** = 1:1	413
	NaN_3, MsOH, CH_2Cl_2, 0°, 2 h	 (15) +  (10)	414
	NaN_3, MsOH, 0°, 10 min	 (—) +  (—)	81

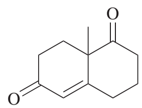
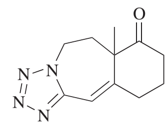
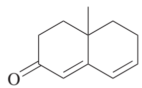
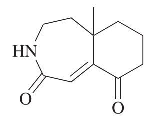
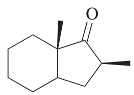
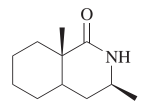
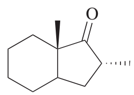
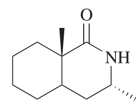
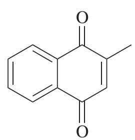
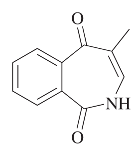
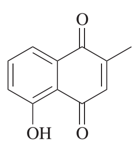
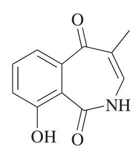
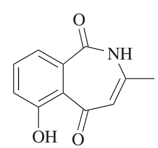
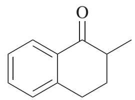
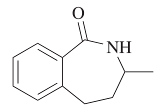
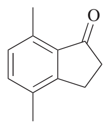
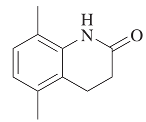
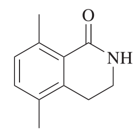
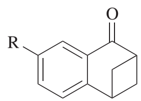
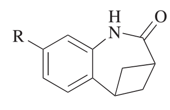
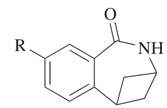
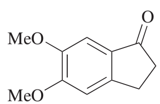
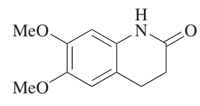
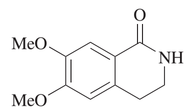
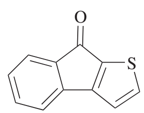
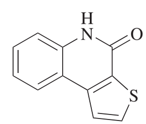
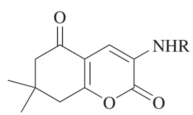
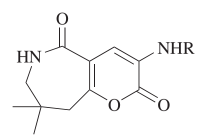
	NaN_3 (2 eq), HCl (concd), rt, 1 h	 (35)	415
	NaN_3, PPA, rt, 4 h	 (20)	416
	NaN_3, H_2SO_4, PhH, 0°, 30 min	 (27)	119
	NaN_3, H_2SO_4, PhH, 0°, 30 min	 (31)	119
	NaN_3, H_2SO_4, 0°, 1 h	 (85)	71
	NaN_3, H_2SO_4, 0°, 1 h	 (56) +  (10)	417

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	NaN_3, HCl, 0° to rt, 4 h	 (34)	397
	NaN_3, PPA, 60°	 (24) +  (41)	387
	NaN_3, H_2SO_4, PhH, 60°, 12 h	 **I** +  **II** R / **I** / **II** H (68) (23) H_2N (56) (24) O_2N (64) (16)	418
	$TMSN_3$, MsOH, MsCl, <0°	 **I** +  **II** **I** + **II** (90), **I**:**II** = 1:1	384
	HN_3, CCl_3CO_2H, H_2SO_4, 55°	 (—)	419
	NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 4 h	 R H (71) PhCO (91)	420

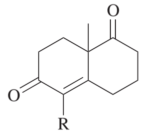
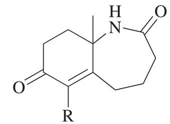
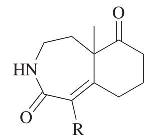
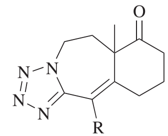
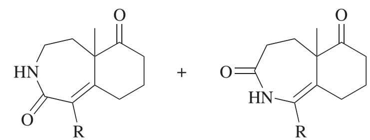
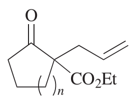
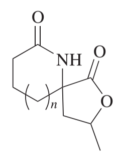
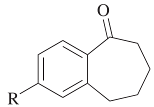
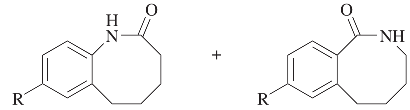
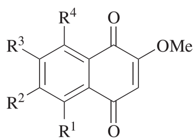
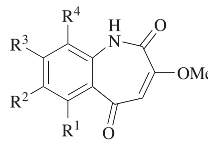
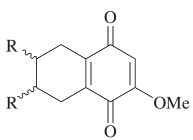
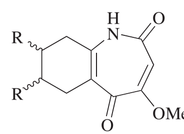
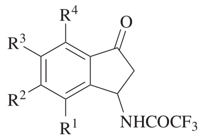
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12} 	NaN_3 (2 eq), H_2SO_4, 5°, 1 h	 R: H (46); Me (35)	415
	NaN_3 (1 eq), HCl (concd), rt, 45 min	 R: H (47); Me (25)	415
	NaN_3 (2 eq), HCl (concd), rt, 1 h	 (35)	415
	NaN_3 (3 eq), CCl_3CO_2H,[b] 60°, 2.5 h	 **I** + **II**; R: H, **I** (0), **II** (20); Me, **I** (6), **II** (0)	415
	NaN_3, H_2SO_4, $CHCl_3$, rt, 1 h	 *n*: 1 (65); 2 (60)	415a

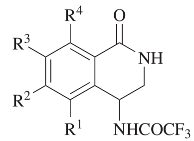
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12}			
	A: NaN_3, H_2SO_4, PhH, 60° B: NaN_3, CCl_3CO_2H,[b] 65° C: NaN_3, HCl, DME, rt D: NaN_3, concd HCl	 **I** + **II**	
		R / Conditions / **I + II** / **I:II**	
		H / A / (—) / 4:1	59
		H / B / (—) / 4:1	59
		H / C / (83) / 1:0	421
		H / D / (89) / 1:0	422
		MeO / A / (—) / 4:1	59
		MeO / B / (—) / 4:1	59
C_{11-13}			
	NaN_3, H_2SO_4, 0° to rt, 24 h		423
		R^1 / R^2 / R^3 / R^4	
		H / H / H / H	
		H / H / H / Me	
		Me / H / H / H	
		H / Me / H / Me	
		H / Me / Me / H	
		Me / H / H / Me	
		Me / H / Me / H	
		Me / Me / H / H	
	NaN_3, H_2SO_4, rt, 16 h		424
		R	
		H (19)	
		Cl (16)	
		Me (6)	

C_{11-14}

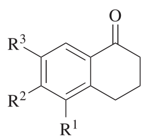


NaN$_3$, TFA, reflux, 5 h

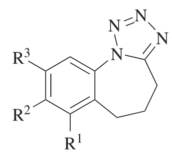


R^1	R^2	R^3	R^4	
H	H	H	H	(62)
H	F	H	H	(67)
H	H	F	H	(56)
Br	H	H	H	(69)
Cl	Cl	H	H	(73)
Me	H	H	H	(69)
H	Me	H	H	(66)
H	H	Me	H	(54)
Me	H	Me	H	(71)
H	H	Et	H	(59)
H	H	*i*-Pr	H	(64)

425



NaN$_3$, BF$_3$•OEt$_2$, PhH, rt, 24 h

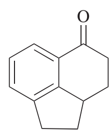


(50–70)

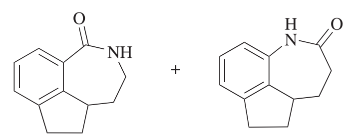
R^1	R^2	R^3
H	H	MeO
H	MeO	MeO
H	MeO	EtO
H	EtO	MeO
H	EtO	EtO

396

C_{12}



NaN$_3$, PPA, 80°, 5 h

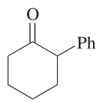
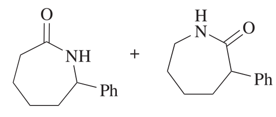
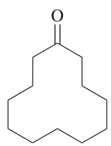
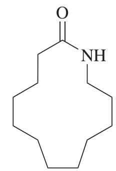
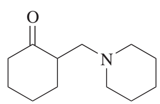
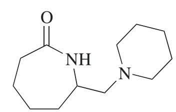
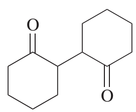
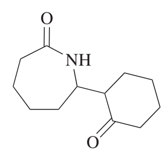


I **II**

I + II (54), **I**:**II** = 1:1.5

426

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	A: NaN_3, PPA, rt, 18 h B: NaN_3, PPA, rt to 55° C: NaN_3, H_2SO_4, $CHCl_3$, 0°, 3 h D: NaN_3, PPA, 0°, 3 h E: NaN_3, H_2SO_4, Et_2O, rt, 3 h F: NaN_3, H_2SO_4, PhH, rt, 3 h	 **I** + **II** Conditions / **I + II** / **I:II** A (40) 1:10 B (30) 1:3 C (60) 1:2 D (40) 0:100 E (15) 1.3:1 F (15) 100:0	368 368 296 296 296 296
	A: NaN_3, silica sulfuric acid,[a] 60°, 30 min B: NaN_3, P_2O_5, MW, 7 min C: NaN_3, $Fe(HSO_4)_3$, grinding, 50°, 30 min	 **I** Conditions A (95) B (75) C (94)	 282 289 288
	Azide, $FeCl_3$, DCE, rt	**I** Azide / Time $TMSN_3$ 65 min (81) NaN_3 4 h (65)	286
	NaN_3, HCl (concd), rt	 (63)	333
	NaN_3, PPA, 15° to rt, 15 h	 (29)	427

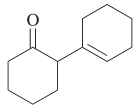
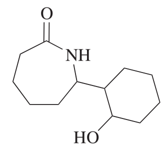
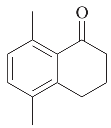
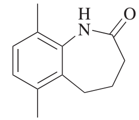
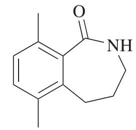
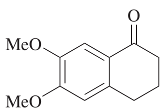
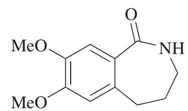
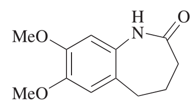
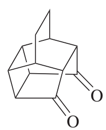
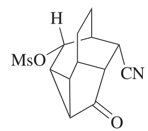
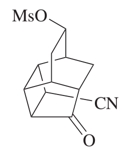
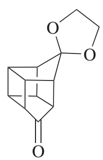
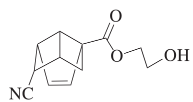
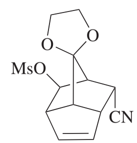
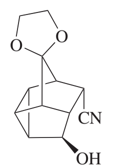
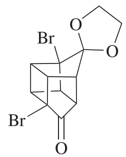
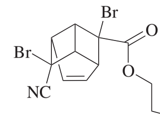
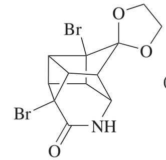
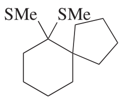
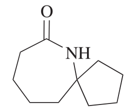
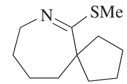
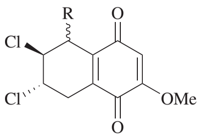
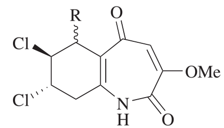
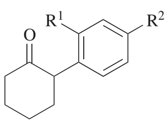
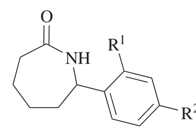
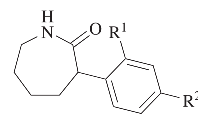
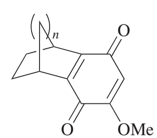
	NaN_3, PPA, 15° to rt, 15 h	 (60)	428
	NaN_3, PPA, 60°	 (43) +  (19)	387
	NaN_3, HCl (concd), 0° to rt, 12 h	 (69) +  (26)	429
	NaN_3, MsOH, CH_2Cl_2, 0°, 30 min	 (45) +  (15)	430
	NaN_3, MsOH, 0°, 1 h	 (16) +  (10) +  (5)	431

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

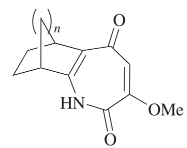
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	NaN_3, MsOH, 0°, 1 h	 (16) +  (20)	431
	1. IN_3, CH_2Cl_2, –78 to –10°, 2 h 2. TFA, $CHCl_3$, rt, 2 h	 (47)	83
	$TMSN_3$, $SnCl_4$, I_2, CH_2Cl_2, –78°, 2.5 h	 (41)	83
$C_{12–13}$			
	NaN_3, TFA, 0° to rt, 2.5 h	 R: Me (31); Et (41)	424
	A: NaN_3, PPA, 0°, 6 h B: NaN_3, H_2SO_4, PhH, rt, 6 h C: NaN_3, H_2SO_4, Et_2O, 0°, 6 h	 **I** +  **II**	296

Conditions	R^1	R^2	**I**	**II**
A	H	H	(60)	(—)
B	H	H	(—)	(40)
C	H	H	(—)	(30)
A	H	O_2N	(16)	(64)
B	H	O_2N	(25)	(45)
C	H	O_2N	(—)	(65)
A	O_2N	H	(17)	(68)
B	O_2N	H	(28)	(47)
C	O_2N	H	(39)	(31)
A	O_2N	O_2N	(—)	(55)
B	O_2N	O_2N	(—)	(80)
C	O_2N	O_2N	(—)	(42)
A	H	Me	(10)	(—)
B	H	Me	(40)	(5)
C	H	Me	(15)	(15)
A	H	MeO	(10)	(—)
B	H	MeO	(5)	(—)
C	H	MeO	(11)	(4)

C_{12-13}

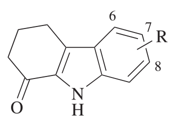


NaN_3, H_2SO_4, 0°, 2 min

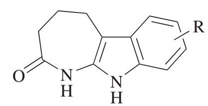


n	
1	(1.4)
2	(31)

424



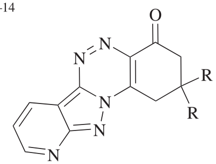
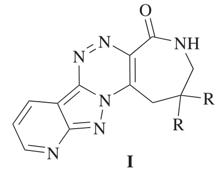
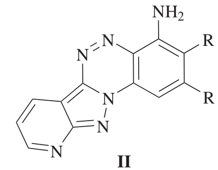
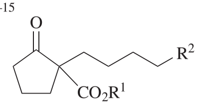
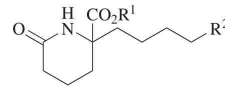
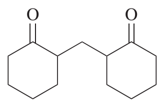
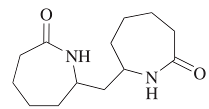
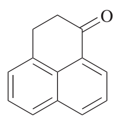
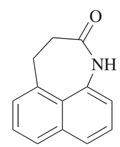
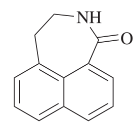
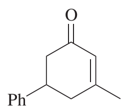
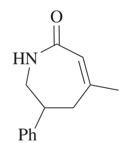
NaN_3, PPA, 100°, 8 h



R	
H	(45)
6-Cl	(57)
6-Me	(49)
7-Me	(44)
8-Me	(58)

432

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-14} 	NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h	 **I** +  **II** R / **I** / **II** H (16) (13) Me (6) (17)	433
C_{12-15} 	NaN_3, H_2SO_4, $CHCl_3$	 R^1 / R^2 Me NC– (48) Et EtO_2C (87)	434
C_{13} 	A: NaN_3, HCl, 0°, 30 min B: NaN_3, PPA, rt, 24 h	 Conditions A (57) B (80)	435
	NaN_3, H_2SO_4, 0°	 (37) +  (—)	436
	NaN_3, PPA, 0–55°, 7 h	 (30)	368

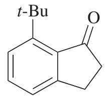
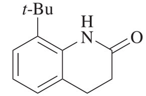
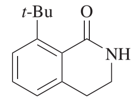
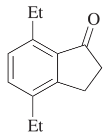
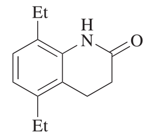
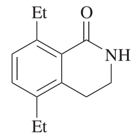
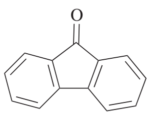
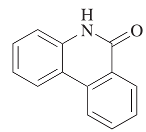
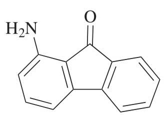
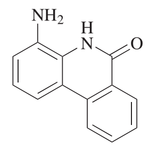
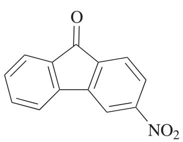
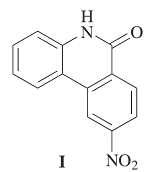
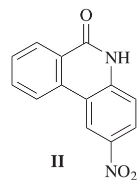
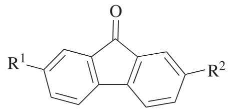
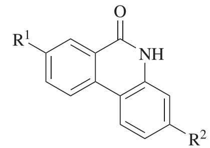
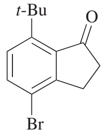
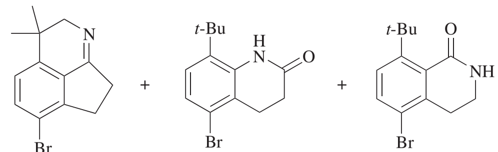
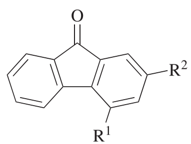
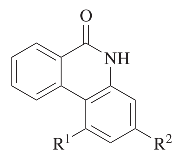
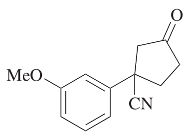
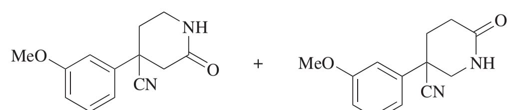
C_{13}			
	NaN_3, PPA	 (5) +  (20)	437
	NaN_3, PPA, 60°	 (10) +  (25)	387
	A: NaN_3, PPA, 70°, 22 h B: NaN_3, CCl_3CO_2H,[b] 60° C: NaN_3, H_2SO_4	 Conditions: A (92); B (55); C (99)	54 1 1
	NaN_3, H_2SO_4	 (80)	438
	NaN_3, H_2SO_4, $CHCl_3$	 **I** +  **II** **I** + **II** (98), **I**:**II** = 7:3	439

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	NaN_3, H_2SO_4, 0° to rt, 24 h	 R[1] / R[2]: Cl / H_2N (61); Cl / O_2N (80); Br / H_2N (55); Br / O_2N (100)	440
	NaN_3, PPA, 50°, 9 h	 (20) + **I** + **II** **I + II** (47), **I:II** = 85:15	387
	NaN_3, H_2SO_4, 0° to rt, 48 h	 R[1] / R[2]: H_2N / H (99); O_2N / H (96); Cl / O_2N (71)	440
	NaN_3, CCl_3CO_2H[b]	 **I** + **II** **I + II** (—), **I:II** = 2:3	441
	NaN_3, 80% H_2SO_4, PhH	**I + II** (—), **I:II** = 100:0	441

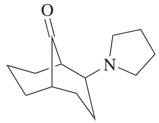
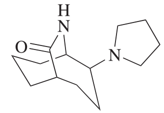
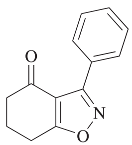
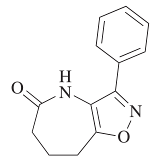
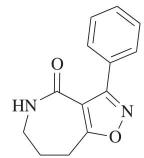
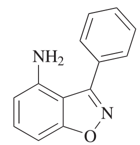
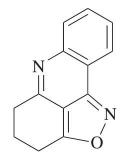
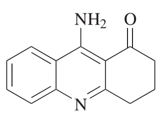
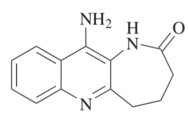
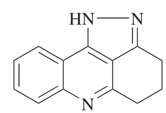
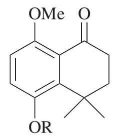
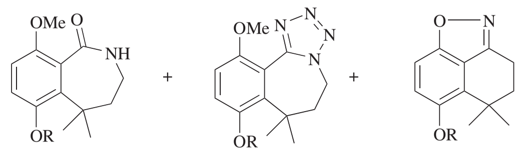
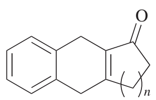
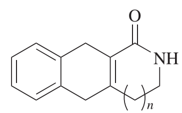
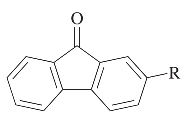
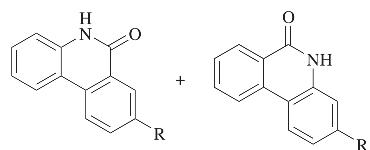
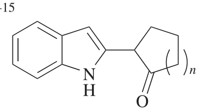
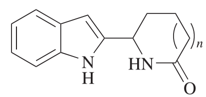
	NaN_3, 98% H_2SO_4, PhH	**I** + **II** (—), **I**:**II** = 2:3	441
	NaN_3, 98% H_2SO_4, $CHCl_3$	**I** + **II** (—), **I**:**II** = 100:0	441
	NaN_3, PPA	**I** + **II** (—), **I**:**II** = 1:1	441
	NaN_3, H_2SO_4, $CHCl_3$, 50°, 1 h	 (56)	442
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 3 h	 (31) +  (4) +  (30) +  (2)	443
	NaN_3, H_2SO_4, $CHCl_3$, rt, 8 h	 (60) +  (16)	444

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13-14} 	NaN_3, H_2SO_4, $CHCl_3$, 70°, 8 h	 **I** + **II** + **III** R / **I** / **II** / **III** H / (36) / (28) / (0) Me / (51) / (18) / (8)	445
	NaN_3, PPA, 100°, 3 h	 *n* 1 (65) 2 (58)	446
	NaN_3, H_2SO_4, $CHCl_3$, rt, 1 h	 **I** + **II** R / **I + II** / **I:II** O_2N / (—) / 1:1 MeO / (—) / 19:1	439
C_{13-15} 	NaN_3, H_2SO_4, $CHCl_3$, rt	 *n* 1 (62) 2 (57) 3 (48)	341

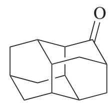
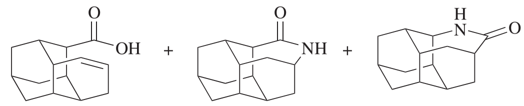
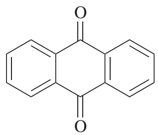
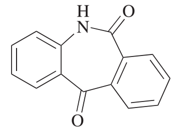
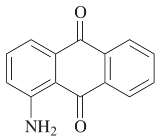
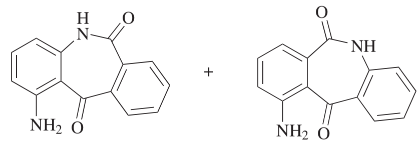
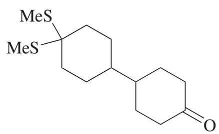
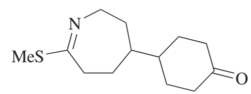
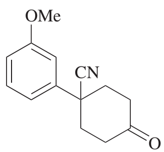
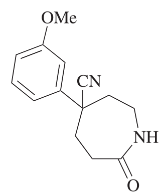
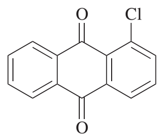
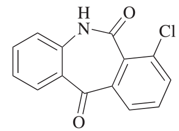
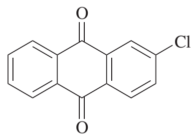
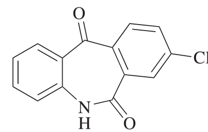
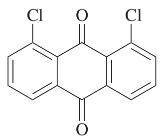
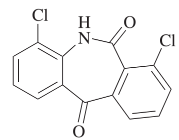
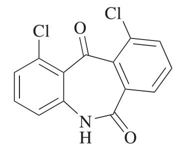
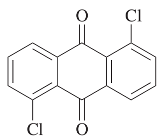
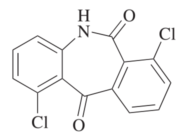
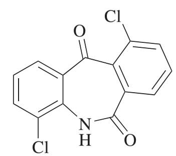
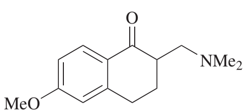
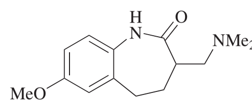
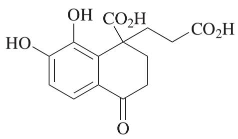
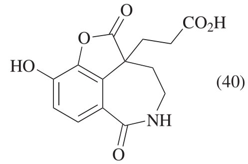
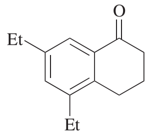
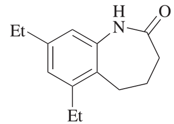
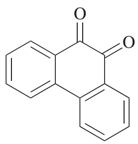
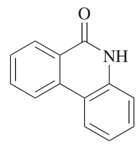
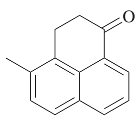
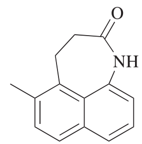
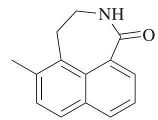
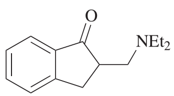
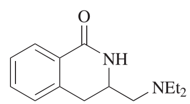
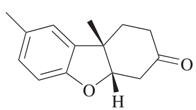
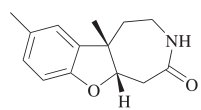
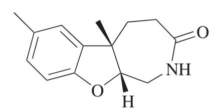
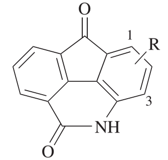
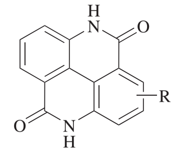
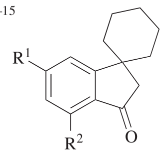
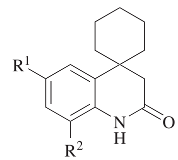
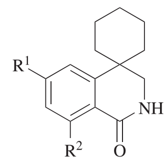
C_{14}			
	NaN_3, MsOH, rt, 2.5 h	 (41) + **I** + **II**; **I + II** (50)	447
	NaN_3, H_2SO_4	 (77)	450
	NaN_3, H_2SO_4, rt, 4 h	 **I** + **II**; **I + II** (80), **I**:**II** = 35:65	448
	$TMSN_3$, $SnCl_4$, I_2, CH_2Cl_2, –78° to rt, 2.5 h	 (90)	83
	NaN_3, CCl_3CO_2H,[b] 60°, 4 h	 (88)	449

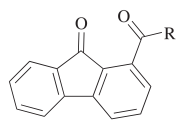
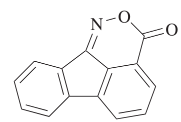
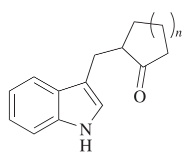
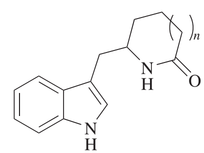
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (10) + isomers (4)	450
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (8) + isomers (8)	450
	NaN_3, H_2SO_4, 50°, 4 h	 **I** +  **II** **I** + **II** (90)	451
	NaN_3, H_2SO_4, 50°, 4 h	 **I** +  **II** **I** + **II** (95)	451
	NaN_3, H_2SO_4, rt, 16 h	 (55)	62

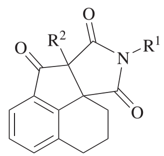
	NaN_3, PPA, 60°, 6 h	 (40)	452
	NaN_3, H_2SO_4	 (—)	12
	NaN_3, H_2SO_4, 0° to rt, 3 h	 (92)	453
	NaN_3, H_2SO_4, AcOH, 50°, 1 h	 (50) +  (6)	454
	NaN_3, HCl (concd)	 (—)	333
	NaN_3, PPA, 40°, 1 h	 (38) +  (56)	455

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	NaN_3, H_2SO_4, 50°, 4 h	 R: H (86); 1-O_2N (—); 3-O_2N (—)	456
C_{14-15} 	A: NaN_3, H_2SO_4, PhH, 60° B: NaN_3, CCl_3CO_2H,[b] 65°	 **I** +  **II**	

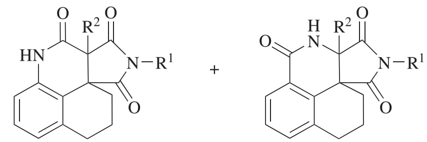
R^1	R^2	Conditions	**I + II**	**I:II**	Refs.
H	H	A	(83)	7:3	457
H	H	B	(—)	1:4	59
MeO	H	A	(78)	1:9	457
MeO	H	B	(—)	1:9	59
H	MeO	A	(66)	1:9	457
H	MeO	B	(—)	1:9	59

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3, H_2SO_4	 R: HO (—); MeO (—)	458
	NaN_3, H_2SO_4, 0 to 50°, 5 h	 n: 1 (70); 2 (74)	459

C$_{14-16}$



A: NaN_3, H_2SO_4, rt
B: NaN_3, PPA, 80°, 15 h

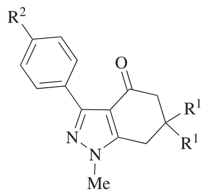


I + **II**

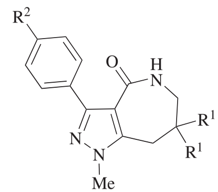
R^1	R^2	Conditions	**I**	**II**
H	H	A	(91)	(0)
H	H	B	(45)	(30)
Me	H	A	(87)	(0)
Me	H	B	(47)	(48)
Me	Me	A	(74)	(0)
Me	Me	B	(43)	(28)

460

C$_{14-17}$



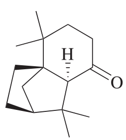
HN_3, H_2SO_4, PPA, rt, 0.5 h



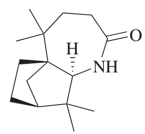
R^1	R^2	
H	H	(62)
H	Cl	(31)
Me	H	(61)
H	MeO	(26)
Me	Cl	(20)
Me	O_2N	(21)
Me	MeO	(27)

461

C$_{15}$



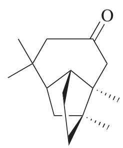
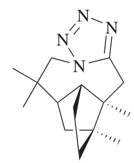
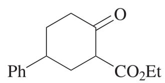
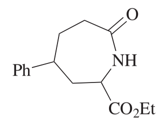
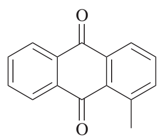
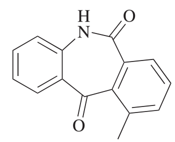
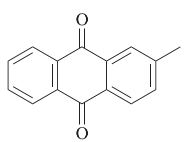
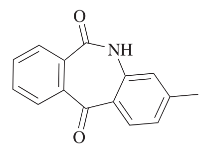
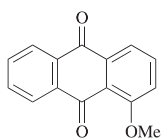
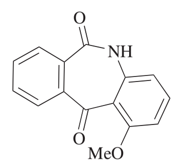
NaN_3, H_2SO_4, $CHCl_3$, 0°, 45 min



(32)

462

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	NaN_3, H_2SO_4, $CHCl_3$, 0°, 45 min	 (42)	462
	A: NaN_3, PPA, rt, 3 h B: NaN_3, H_2SO_4, $CHCl_3$, rt, 48 h	 Conditions: A (74); B (26)	463
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (19) + isomers (23)	450
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (20) + isomers (18)	450
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (63)	450

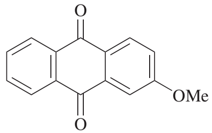
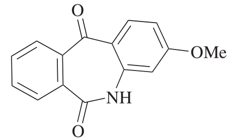
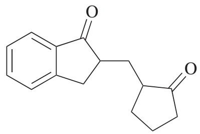
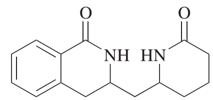
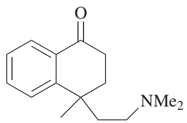
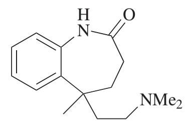
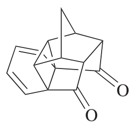
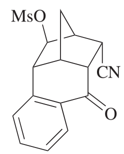
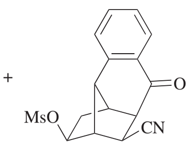
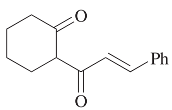
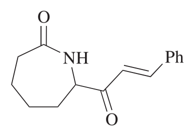
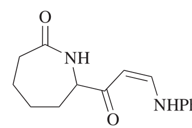
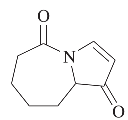
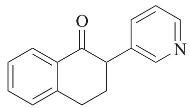
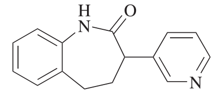
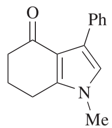
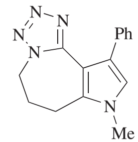
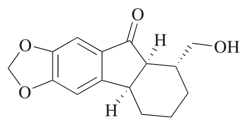
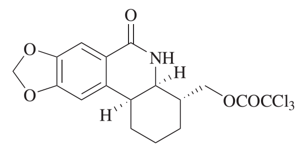
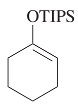
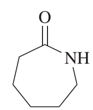
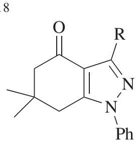
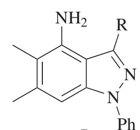
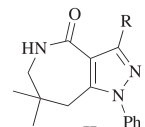
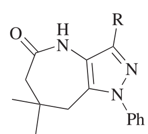
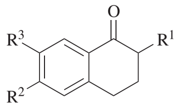
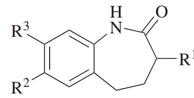
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (22) + isomers (5)	450
	NaN_3, H_2SO_4, $CHCl_3$, 0°, 1 h	 (58)	464
	NaN_3, PPA, 60°, 24 h	 (93)	58
	NaN_3, MsOH, 0°, 45 min	 (—) +  (—)	465
	NaN_3 (1 eq), H_2SO_4	 (50) +  (6) +  (5)	412

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	NaN_3, H_2SO_4, AcOH, 50°, 0.5 h; rt, 1 h	 (34)	466
	NaN_3, H_2SO_4, $CHCl_3$, rt, 30 min	 (34)	392
	NaN_3, CCl_3CO_2H,[b] 60°, 60 h	 (55)	467
	1. $TMSN_3$, Dowex, CH_2Cl_2, rt, 48 h 2. *h*ν, *c*-C_6H_{12}, 0°, 3.5 h	 (83)	468
C_{15-18}			
	NaN_3, PPA, 60°, 12 h	 **I** +  **II** +  **III** **I** + **II** + **III** (—) R — **I**:**II**:**III** H — 0:100:0 Me — 18:61:21 *i*-Pr — 17:67:16	469



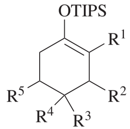
NaN$_3$, AcOH, 50°, 2 h



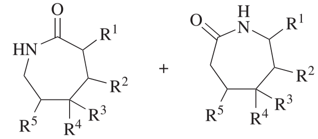
R^1	R^2	R^3	
3-C$_5$H$_4$N	H	H	(66)
Ph	Cl	H	(33)
Ph	MeO	MeO	(44)

470

C$_{15-19}$



1. TMSN$_3$, PPTS, CH$_2$Cl$_2$, rt, 2 d
2. $h\nu$, c-C$_6$H$_{12}$, 0°, 1 h

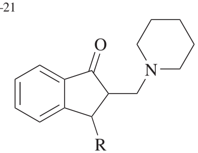


I + **II**

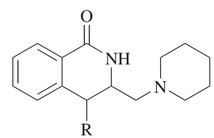
R^1	R^2	R^3	R^4	R^5	**I**	**II**
H	H	H	H	H	(69)	(0)
Me	H	H	H	H	(20)	(12)
H	H	H	H	Me	(36)	(36)
H	H	Me	H	H	(68)	(0)
H	H	Me	Me	H	(60)	(0)
H	H	–O(CH$_2$)$_2$O–		H	(77)	(0)
H	H	t-Bu	H	H	(63)	(0)

74

C$_{15-21}$



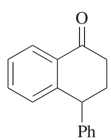
NaN$_3$, HCl



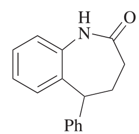
R	
H	(—)
Ph	(—)

333

C$_{16}$



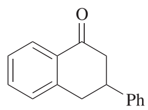
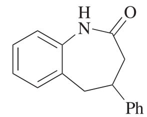
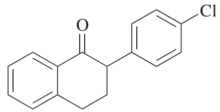
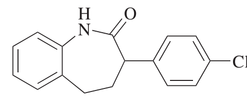
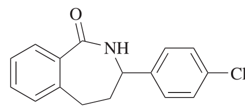
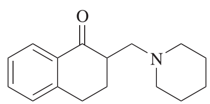
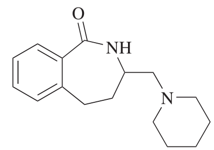
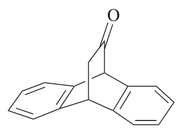
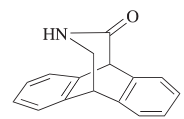
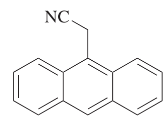
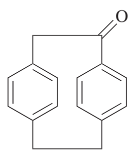
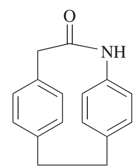
NaN$_3$, AcOH, 50°, 2 h



(84)

470

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	NaN_3, H_2SO_4, AcOH, 50°, 45 min	 (61)	471
	NaN_3, AcOH, rt to 50°, 3 h	 (42) +  (—)	472
	NaN_3, HCl (concd)	 (—)	333
	NaN_3, CCl_3CO_2H,[b] 60°	 (10) +  (35)	473
	NaN_3, H_2SO_4, dioxane, 15–45°, 45 min	 (52)	474

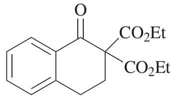
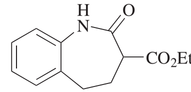
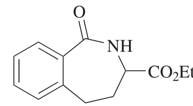
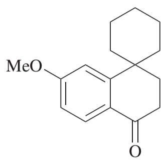
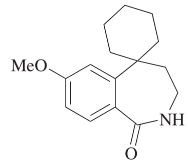
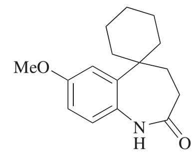
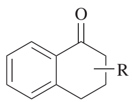
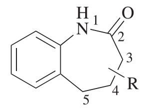
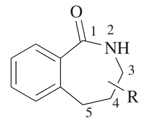
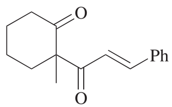
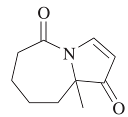
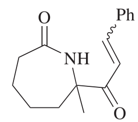
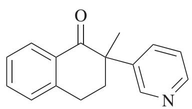
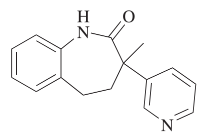
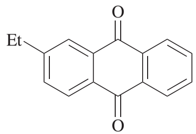
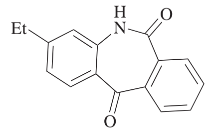
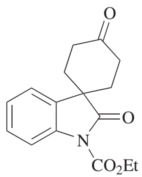
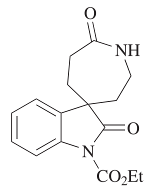
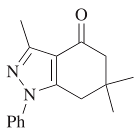
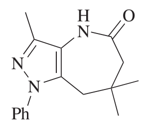
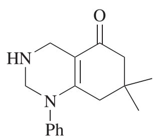
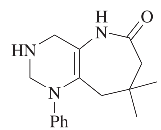
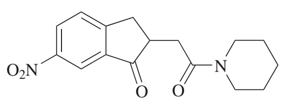
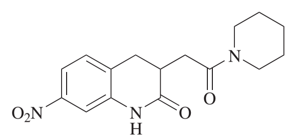
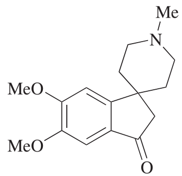
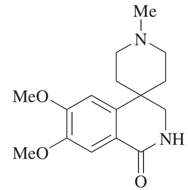
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3, MsOH, $CHCl_3$, reflux, 36 h	 (50) +  (27)	397
	NaN_3, H_2SO_4, PhH, 60°, 8 h	 (28) +  (38)	457
	NaN_3, H_2SO_4, AcOH, rt to 50°, 4 h	 **I** +  **II** R — **I + II** 3-Ph — (—) 4-Ph — (65) 5-Ph — (63) 3-(4-ClC_6H_4) — (47)	475
	NaN_3 (2 eq), H_2SO_4	 (75) +  (*E*) + (*Z*) (traces)	412
	NaN_3, AcOH, 50°, 2 h	 (66)	470

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

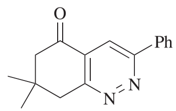
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (22)	450
	NaN_3, H_2SO_4, $CHCl_3$, –10° to rt	 (90)	476
	NaN_3, PPA, 100°, 5 h	 (54)	477
	NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 5 h	 (70)	478
	NaN_3, H_2SO_4, PhH, 40°, 15 min	 (63)	479



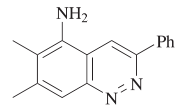
NaN$_3$, H$_2$SO$_4$, 60°, 45 min



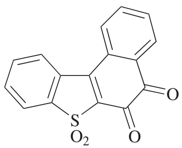
(79) 480



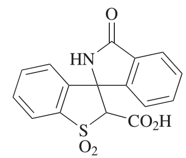
NaN$_3$, H$_2$SO$_4$, rt, 2 h



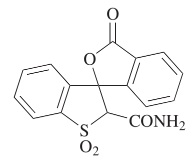
(75) 481



NaN$_3$, H$_2$SO$_4$, 45°, 30 min

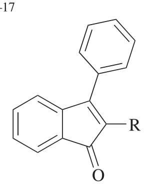


(80) +

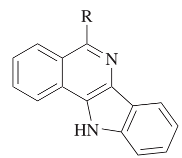


(8) 482

C_{16-17}



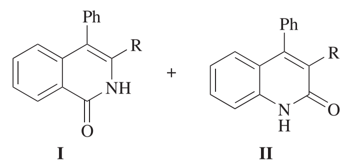
HN$_3$



R	
Me	(—)
Et	(—)

61

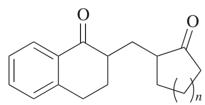
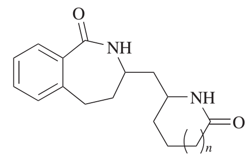
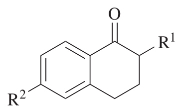
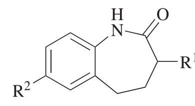
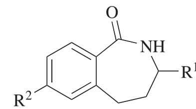
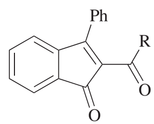
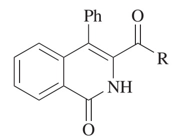
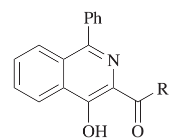
NaN$_3$, AcOH, 50°, 1 h

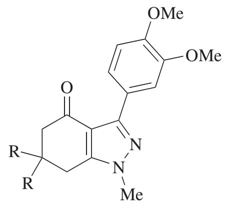


R	**I + II**	**I:II**
Me	(60)	1:3
NC–	(60)	3:1
Et	(70)	0:100

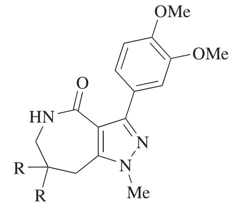
483

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{16–17}$			
	NaN_3, H_2SO_4, rt to 55°, 4.5 h	 *n* — 1 (82); 2 (63)	464
	NaN_3, H_2SO_4, AcOH, 50°, 2 h	 **I** +  **II** R^1 / R^2 / **I** / **II** H / n-C_6H_{13} / (45) / (38) Ph / MeO / (36) / (25)	470
$C_{16–18}$			
	NaN_3, AcOH, rt, 1 h	 R — H_2N (40); EtO (30)	484
	NaN_3, H_2SO_4, rt, 1 h	 R — H_2N (50); EtO (40)	484



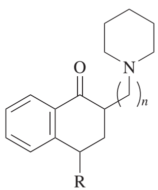
NaN_3, H_2SO_4, PPA, $CHCl_3$, rt, 30 min



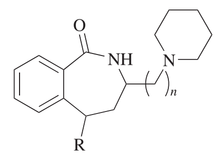
R	
H	(48)
Me	(39)

461

C_{16-22}



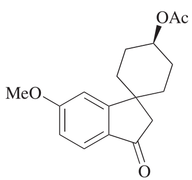
NaN_3, HCl



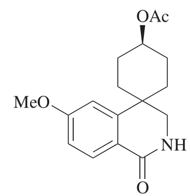
n	R	
1	H	(95)
2	H	(—)
1	Ph	(73)

333

C_{17}

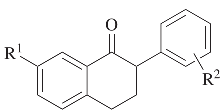


NaN_3, CCl_3CO_2H,[b] 60°, 6.5 h

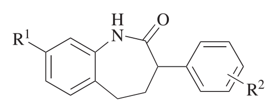


(76)

485



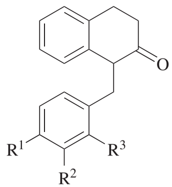
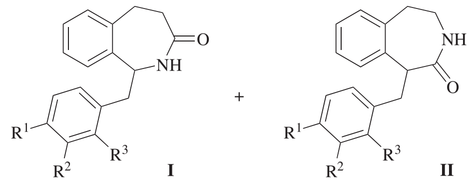
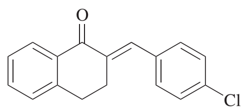
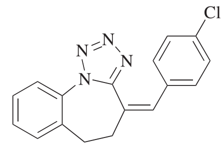
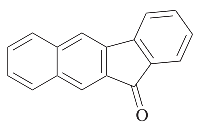
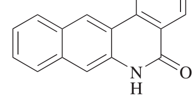
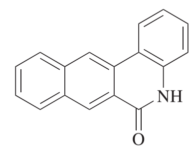
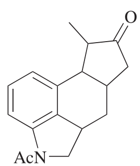
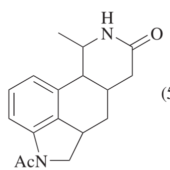
NaN_3, AcOH, 50°, 1 h



R^1	R^2	
H	3-CF_3	(12)
H	4-CF_3	(35)
MeO	H	(40)

466

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	NaN_3, PPA, 40°, 5 h	 I + II R^1 / R^2 / R^3 / I / II H / H / H / (20) / (—) Cl / H / H / (47) / (—) H / H / O_2N / (30) / (—)	461
	NaN_3, $SiCl_4$, MeCN, rt, 18 h	 (80)	70
	NaN_3, H_2SO_4, CCl_3CO_2H,[b] 100°, 4 h	 (23) +  (21)	486
	NaN_3, H_2SO_4, AcOH, 40°	 (56)	487

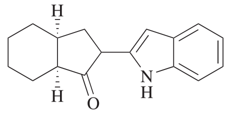
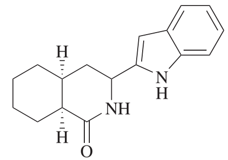
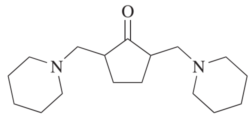
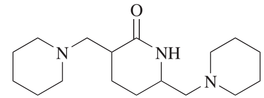
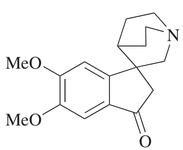
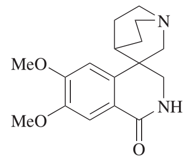
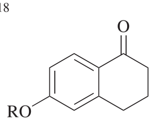
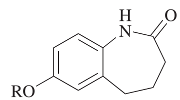
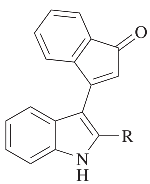
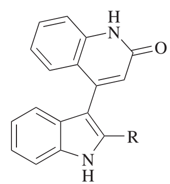
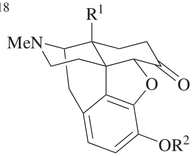
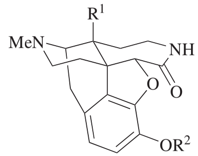
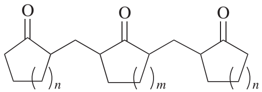
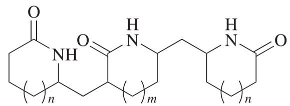
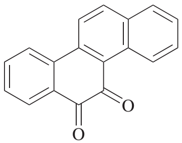
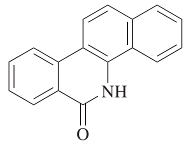
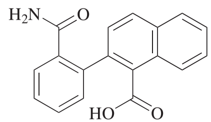
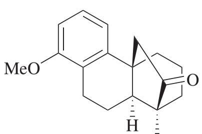
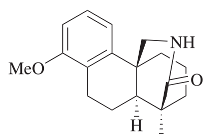
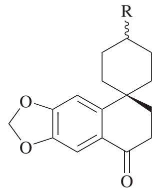
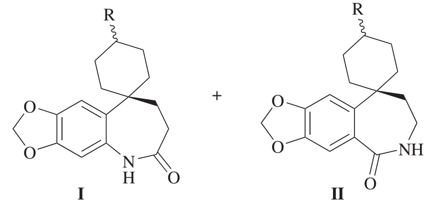
C_{17-18}			
	NaN_3, HCl, H_2SO_4, $CHCl_3$, 0°, 4 h	 (60)	488
	NaN_3, H_2SO_4, 0° to rt, 5 h	 (45)	408
	NaN_3, H_2SO_4, 60°, 45 min	 (90)	480
	NaN_3, H_2SO_4	 R: Bn (71); n-C_8H_{17} (62)	489
	NaN_3, H_2SO_4, $CHCl_3$, 0–50°, rt	 R: H (72); Me (69)	490

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17-18} 	NaN_3, PPA, 65°	 R[1] / R[2]: H / H (40); H / Me (52); HO / Me (23)	491
C_{17-20} 	NaN_3, H_2SO_4, 0 to 55°, 5 h	 *n* / *m*: 1 / 1 (70); 1 / 2 (59); 2 / 1 (66); 2 / 2 (63)	492
C_{18} 	NaN_3, H_2SO_4	 (100)	262
	NaN_3, H_2SO_4, 50°, 1 h	 (70)	262
	NaN_3, H_2SO_4, $CHCl_3$, –10°, 1 h	 (14)	493



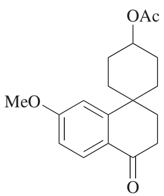
NaN_3, $CCl_3CO_2H^b$



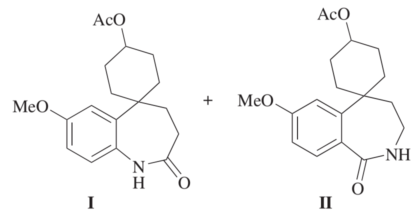
I + II

R	I + II	I:II
α-OAc	(48)	1:1
β-OAc	(59)	1:1

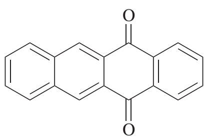
494



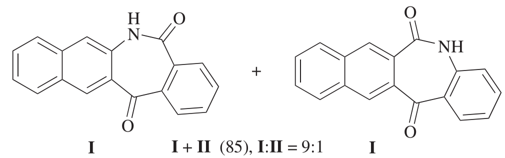
NaN_3, CCl_3CO_2H,[b] 60°, 4 h



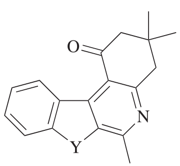
I + II (80), I:II = 2:3 495



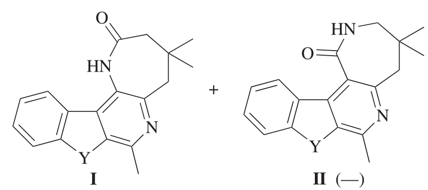
NaN_3, H_2SO_4, rt, 24 h



I + II (85), I:II = 9:1 496



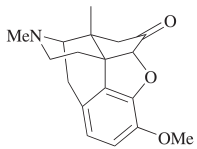
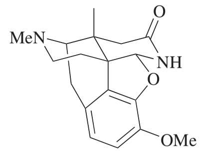
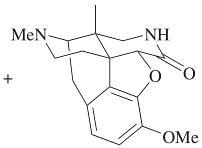
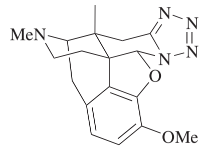
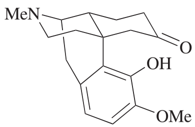
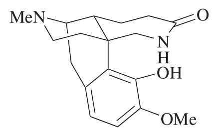
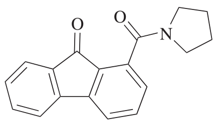
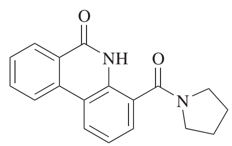
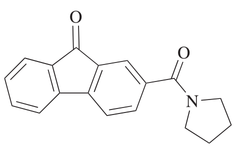
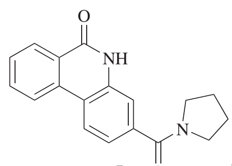
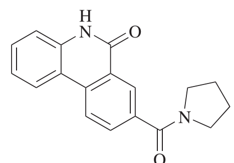
NaN_3, H_2SO_4, rt, 24 h

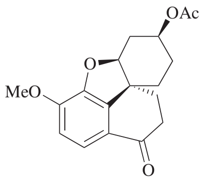


II (—)

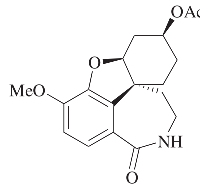
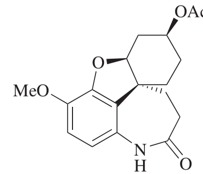
Y	I
HN	(82)
S	(80)

497

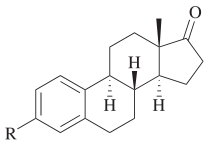
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	NaN_3, P_2O_5, MsOH, 65°, 24 h	 (9) +  (3) +  (15)	498
	NaN_3, PPA, 65°	 (16)	491
	NaN_3, H_2SO_4	 (—)	499
	NaN_3, H_2SO_4, $CHCl_3$, rt, 1 h	 **I** +  **II** **I** + **II** (72)	500



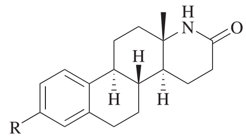
NaN_3, CCl_3CO_2H[b]

 (38) +  (34) 501

C_{18-20}

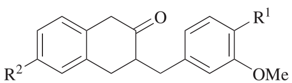


HN_3, H_2SO_4, PhH, rt

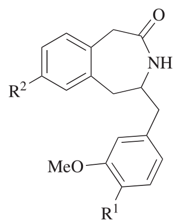


R	
HO	(—)
MeO	(—)
AcO	(—)

502

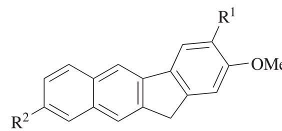


NaN_3, PPA, 70°, 2 h



I

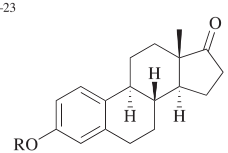
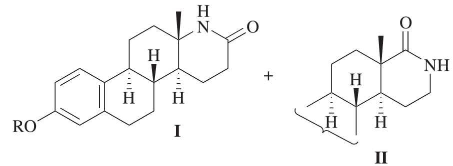
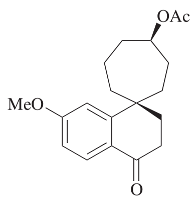
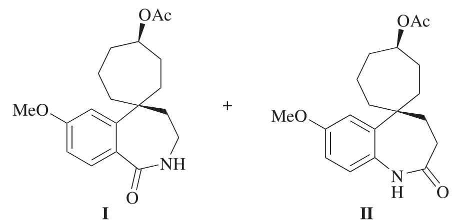
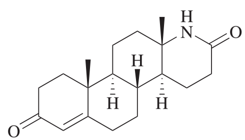
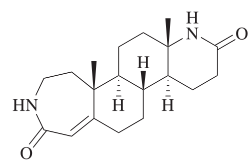
+



II

503

R^1	R^2	**I**	**II**
H	H	(23)	(—)
H	MeO	(45)	(—)
MeO	MeO	(44)	(—)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18-23}			
	A: NaN_3, PPA, 60°, 10 h B: HN_3, H_2SO_4, rt, 2 h	 I + II R / Conditions / I + II / I:II H / A / (—) / 2:1 Me / A / (—) / 1:0 Ac / A / (—) / 1:0 *c*-C_5H_9 / B / (—) / 1:0	504
C_{19}			
	NaN_3, CCl_3CO_2H,[b] 60°, 4 h	 **I** + **II** (79), **I**:**II** = 2:3	505
	NaN_3, PPA, 0°, 20 min	 (35)	506

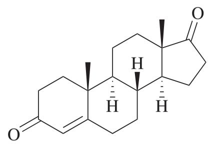
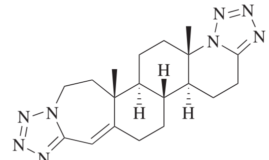
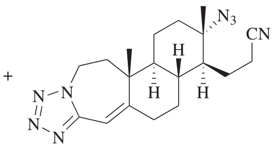
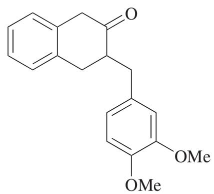
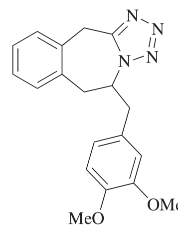
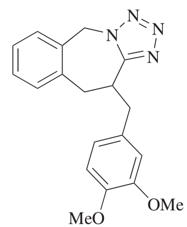
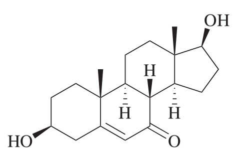
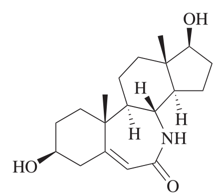
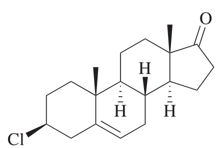
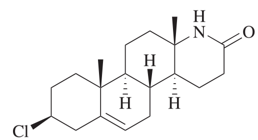
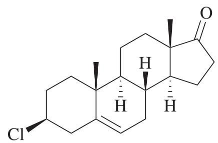
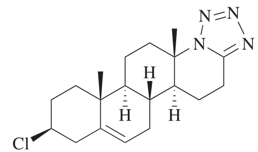
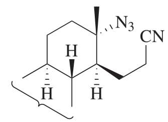
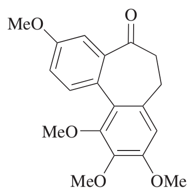
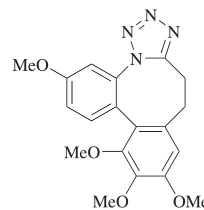
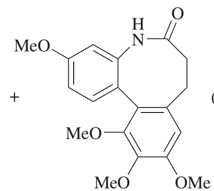
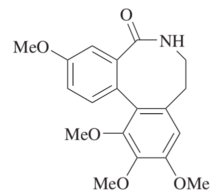
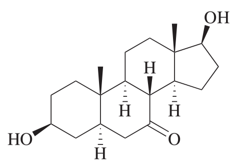
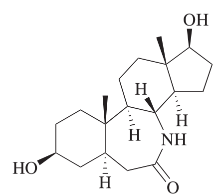
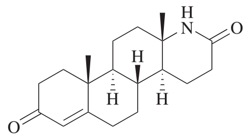
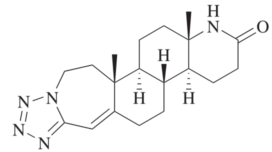
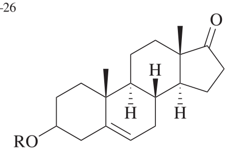
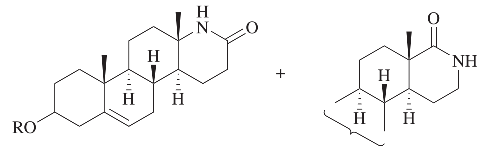
	HN_3, $BF_3 \cdot OEt_2$, $CHCl_3$	 (27) +  (7)	507
	NaN_3, $TiCl_4$, MeCN, reflux, 4 h	 **I** +  **II** **I** + **II** (46), **I**:**II** = 4:1	503
	NaN_3, PPA, 50°, 8 h	 (—)	508
	NaN_3, H_2SO_4, PhH, rt, 30 min	 (60)	34

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	HN_3, BF_3•OEt_2, PhH, 0°, 5 h	 (—) +  (—)	34
	$TMSN_3$, TFA, rt, 24 h	 (68) +  (13) +  (5)	509
	NaN_3, PPA, 50°, 8 h	 (—)	508

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	HN_3, BF_3•OEt_2, $CHCl_3$, 0° to rt, 24 h	 (30)	509a
$C_{19–26}$			
	NaN_3, H_2SO_4, $CHCl_3$, 10°	 **I** + **II**	510

R	I	II
H	(28)	(33)
Ac	(27)	(40)
Bz	(39)	(20)

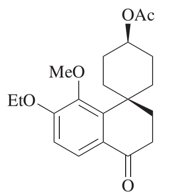
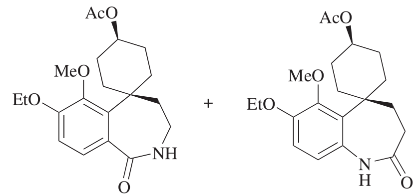
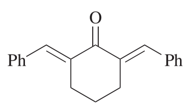
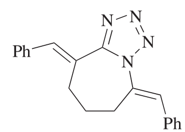
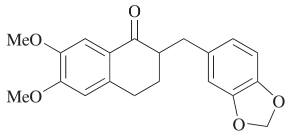
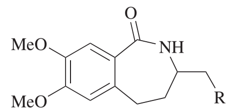
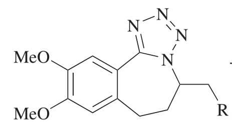
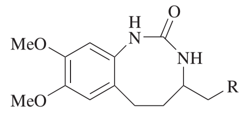
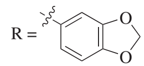
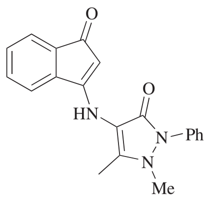
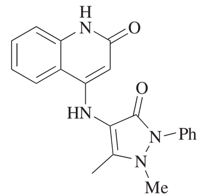
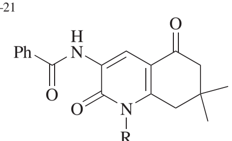
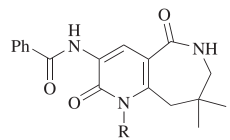
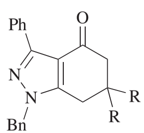
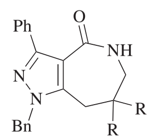
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	NaN_3, CCl_3CO_2H, PhH, 60°, 8 h	 **I** + **II** — **I** + **II** (70), **I**:**II** = 2:3	511
	NaN_3, $SiCl_4$, MeCN, rt, 14 h	 (90)	70

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	NaN_3, CCl_3CO_2H,[b] 57°, 15 h	 (45) +  (12) +  (2) 	512
	NaN_3, H_2SO_4, $CHCl_3$, 0 to 50°, 5 h	 (73)	490
C_{20-21} 	NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 4 h	 R: HO_2CCH_2 (80); MeO_2CCH_2 (84)	420
C_{20-22} 	HN_3, H_2SO_4, $CHCl_3$, rt, 30 min	 R: H (10); Me (10)	461

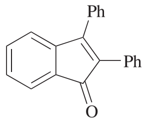
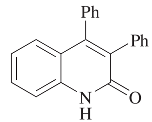
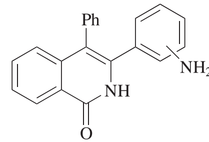
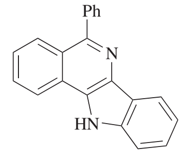
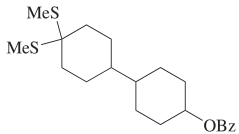
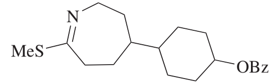
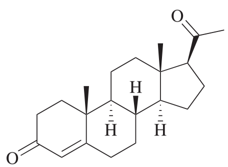
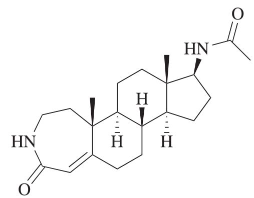
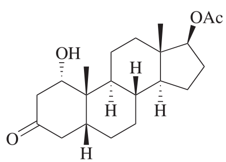
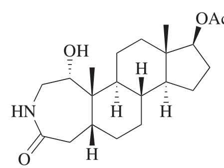
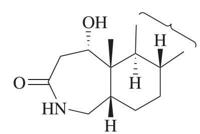
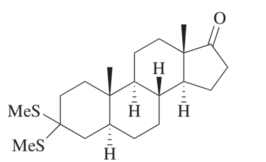
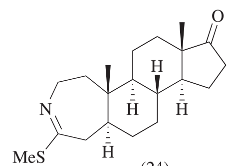
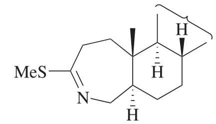
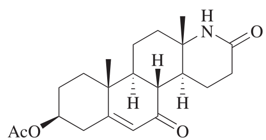
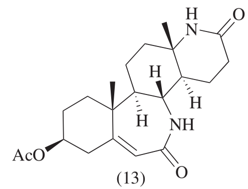
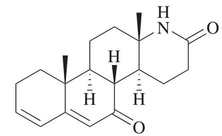
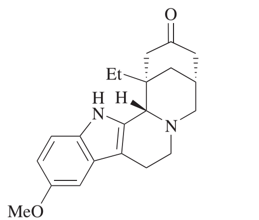
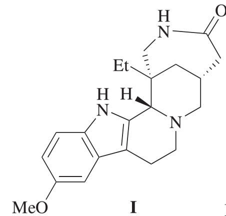
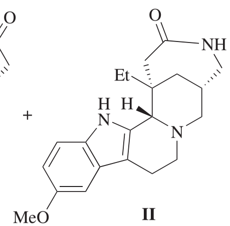
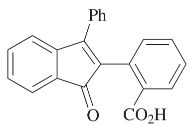
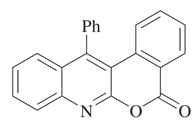
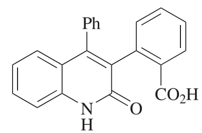
C_{21}			
	NaN_3, AcOH, H_2SO_4	 (40) +  (10) +  (20)	61
	$TMSN_3$, $SnCl_4$, I_2, CH_2Cl_2, –78° to rt, 2.5 h	 (58)	83
	NaN_3, PPA, 50°, 10 h	 (29)	354
	HN_3, H_2SO_4, $CHCl_3$, 0°, 20 min	 (38) +  (18)	513

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	$TMSN_3$, $SnCl_4$, I_2, CH_2Cl_2, –78° to rt, 2.5 h	 (24) +  (24)	83
	NaN_3, PPA, 60°, 10 h	 (13) +  (30)	514
	NaN_3, H_2SO_4, $CHCl_3$	 **I** +  **II** **I** + **II** (85), **I**:**II** = —	515
C_{22}			
	NaN_3, AcOH, 80°, 1 h	 **I** (50) +  **II** (23)	516

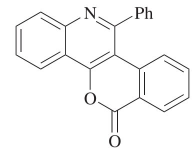
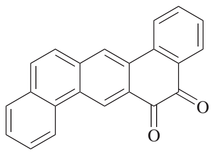
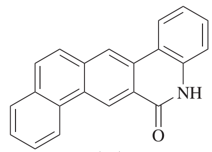
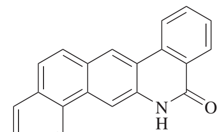
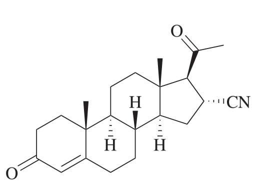
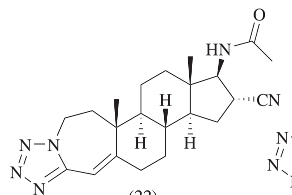
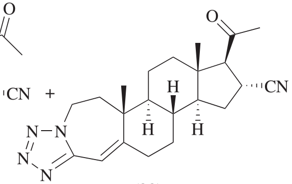
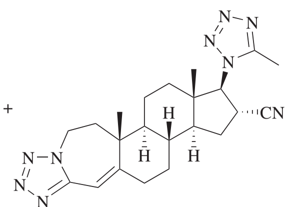
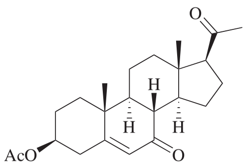
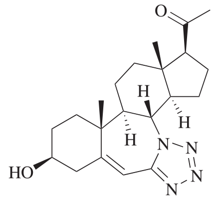
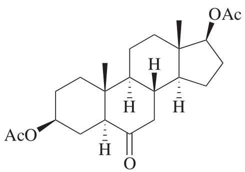
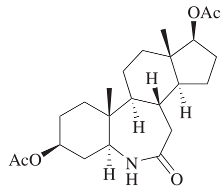
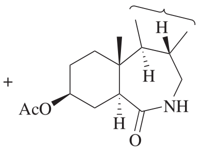
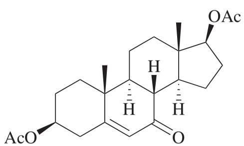
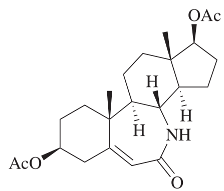
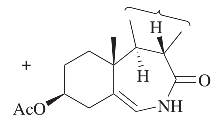
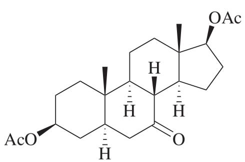
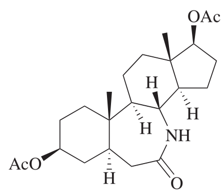
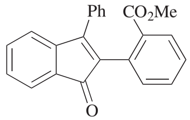
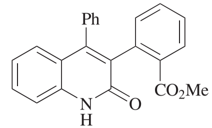
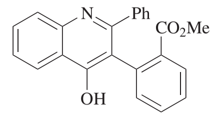
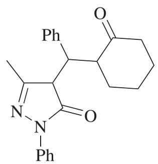
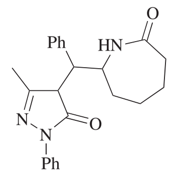
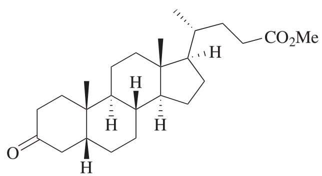
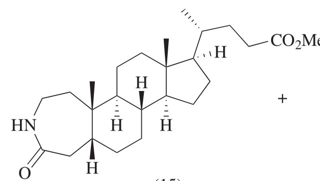
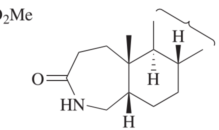
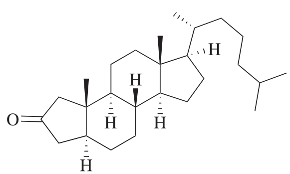
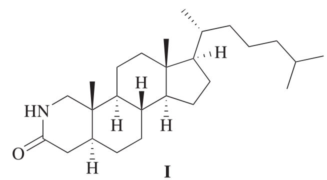
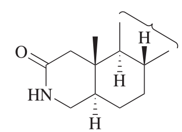
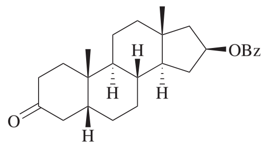
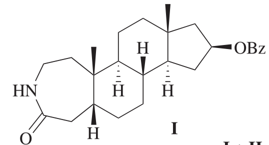
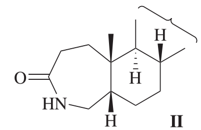
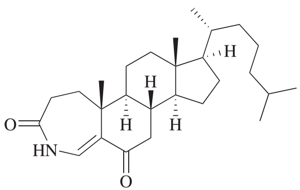
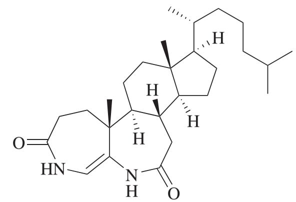
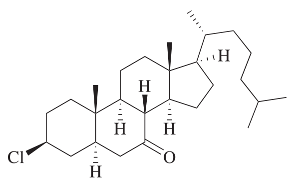
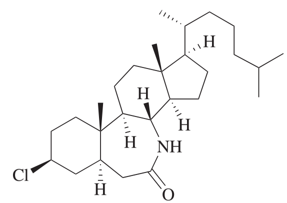
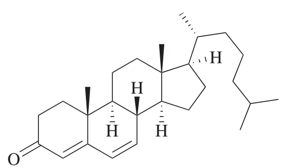
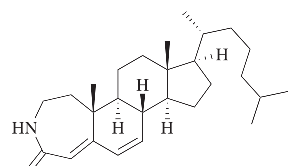
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3, AcOH, H_2SO_4, 40°, 45 min	**I** (25) + **II** (19) +  (15)	516
	NaN_3, H_2SO_4	 (—) +  (—)	453
	HN_3, BF_3•OEt_2, $CHCl_3$, 0° to rt, 24 h	 (22) +  (20) +  (15)	356

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23}			
	HN_3, BF_3•OEt_2, $CHCl_3$, rt, 20 h	 (50)	517
	NaN_3, H_2SO_4, PhH, 20°, 2 h	 (26) +  (22)	508
	NaN_3, PPA, 50°, 8 h	 (26) +  (22)	508
	NaN_3, PPA, 50°, 8 h	 (—)	508

	NaN_3, AcOH, H_2SO_4, 40°, 45 min	 (8) +  (69)	516
	NaN_3, H_2SO_4, $CHCl_3$, 0–50°, 5 h	 (63)	263
C_{25}			
	NaN_3, H_2SO_4, $CHCl_3$, 0°, 30 min	 (15) +  (40)	518
C_{26}			
	NaN_3, PPA, 60°, 10 h	 **I** +  **II** **I + II** (77), **I:II** = —	519

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26}			
	HN_3, H_2SO_4, $CHCl_3$, 0°, 20 min	 **I** +  **II** **I** + **II** (97), **I**:**II** = —	520
	NaN_3, PPA, 60°, 1 h	 (48)	521
C_{27}			
	NaN_3, H_2SO_4, PhH, rt, 1 h	 (50)	522
	NaN_3, H_2SO_4, PhH, rt, 1 h	 **I** (20)	523
	NaN_3, PPA, rt, 2 h	**I** (75)	416

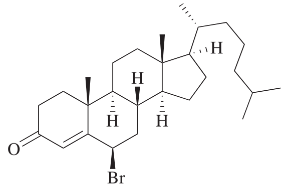
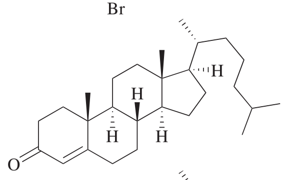
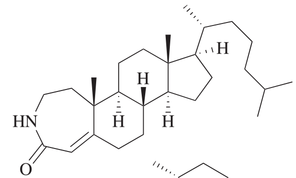
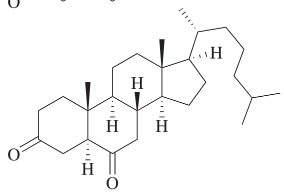
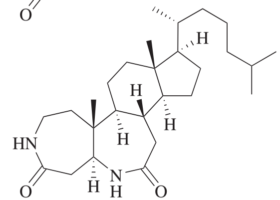
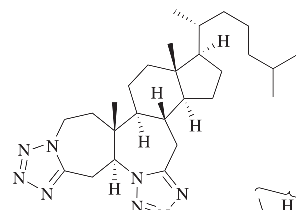
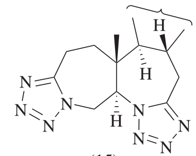
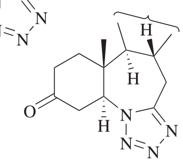
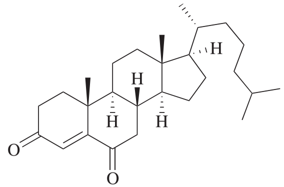
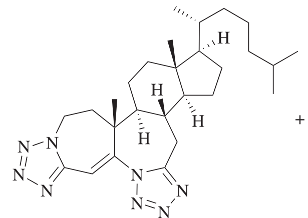
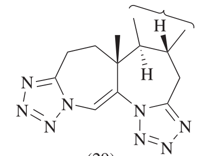
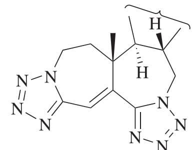
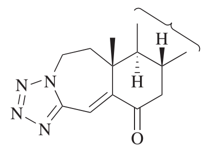
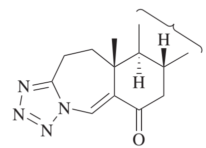
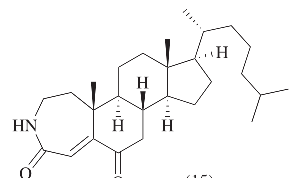
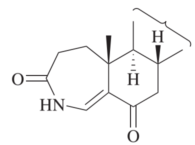
	NaN_3, H_2SO_4, PhH, rt, 1 h	**I** (20)	523
	NaN_3, PPA, 50°, 10 h	 (60)	354
	NaN_3, PPA, 65°, 12 h	 (—)	524
	HN_3, BF_3•OEt_2, PhH, rt, 5 h	 (20) +  (15) +  (10)	525

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27}			
	HN_3, BF_3•OEt_2, $CHCl_3$, 40°, 10 h	 **I** (33) +  (29) +  (11)	526
	HN_3, BF_3•OEt_2, PhH, rt, 5 h	**I** (5) +  (20) +  (10)	525
	NaN_3 (1 eq), PPA, 55°, 10 h	 (15) +  (25)	521

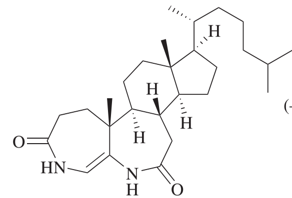
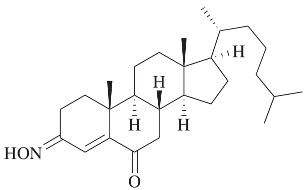
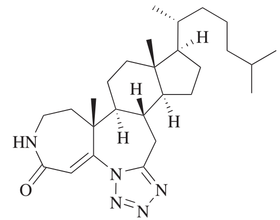
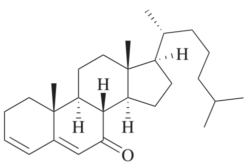
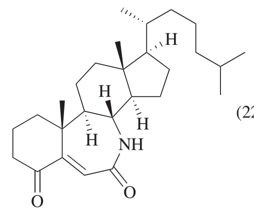
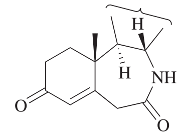
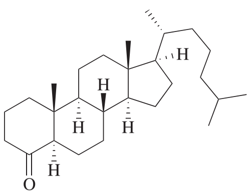
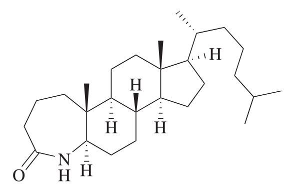
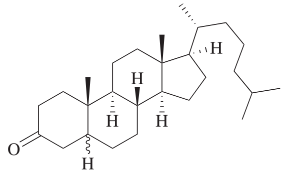
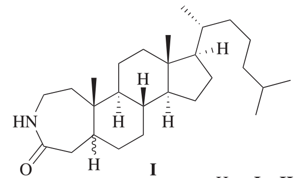
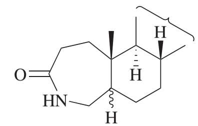
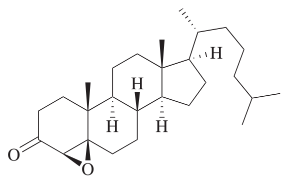
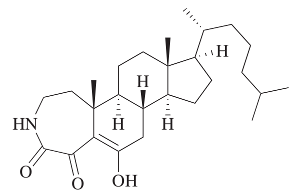
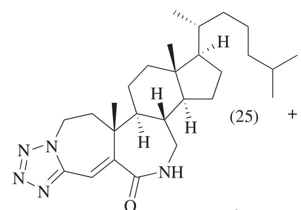
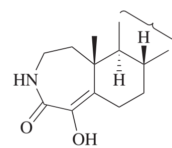
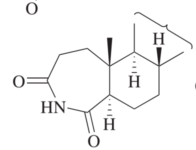
	NaN_3 (2 eq), PPA, 55°, 10 h	 (—)	521
	HN_3, BF_3•OEt_2, $CHCl_3$, 0° to rt, 24 h	 (73)	527
	NaN_3, PPA, rt, 2 h	 (22) +  (12)	416
	NaN_3, PPA, 50°, 6 h	 (25)	528

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27} 	NaN_3, PPA, 65°, 12 h	 I +  II H / I + II / I:II α / (67) / 1:1 β / (86) / 1:1	529
	NaN_3, PPA, 50°, 6 h	 (40)	528
	HN_3, BF_3•OEt_2, PhH, rt, 3 d	 (25) +  (—) +  (10)	530

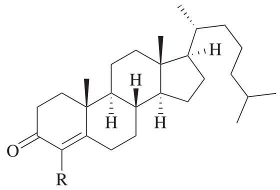
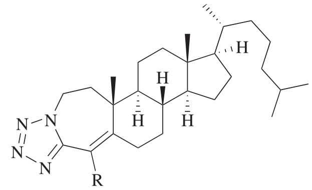
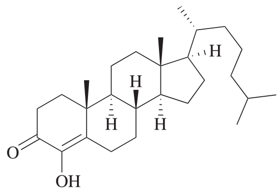
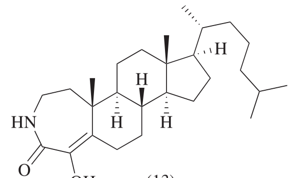
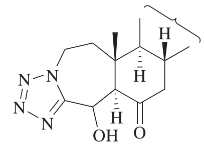
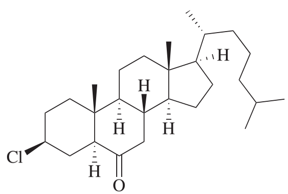
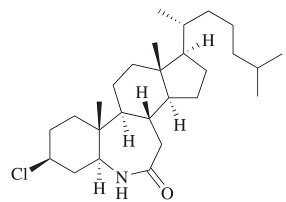
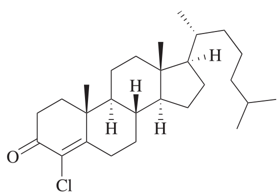
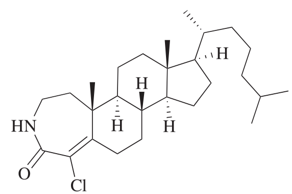
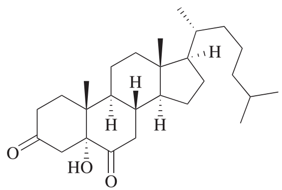
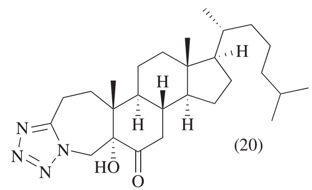
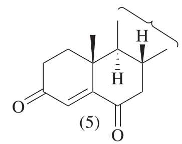
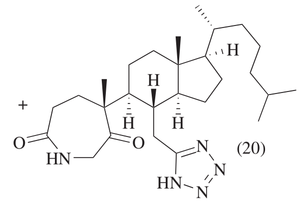
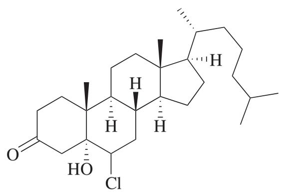
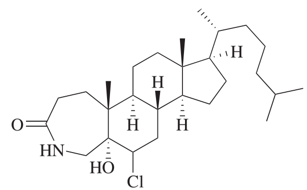
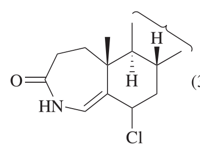
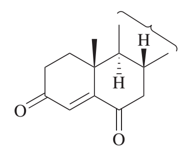
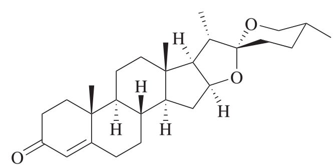
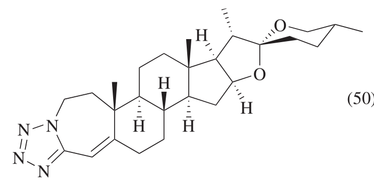
	HN_3, BF_3•OEt_2, PhH, rt, 3 d	 R: Cl (75); Br (70)	530
	HN_3, BF_3•OEt_2, PhH, rt, 3 d	 (13) +  (10)	530[d]
	NaN_3, H_2SO_4, PhH, rt, 1 h	 (50)	531
	NaN_3, PPA, 50°, 6 h	 (50)	528

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27}			
	HN_3, BF_3•OEt_2, PhH, rt, 5 h	 (20) +  (5) +  (20)	525
	HN_3, BF_3•OEt_2, PhH, rt, 24 h	 (30) +  (30) +  (25)	532[d]

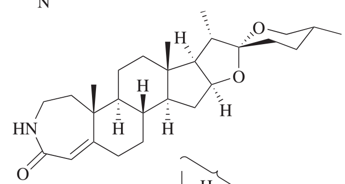


HN_3, BF_3•OEt_2, $CHCl_3$,
0° to rt, 20 h

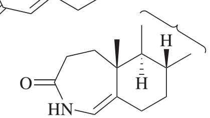


(50) 533

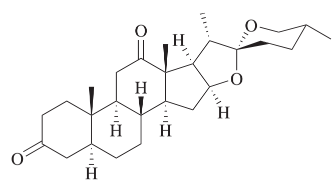
NaN_3, H_2SO_4



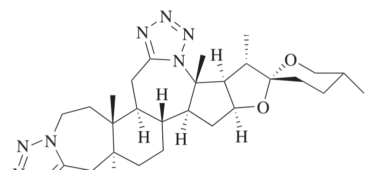
(27) +



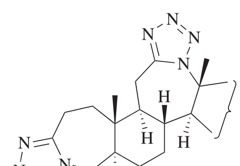
(53) 534



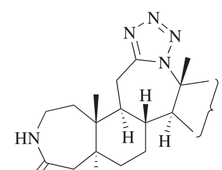
HN_3, BF_3•OEt_2, $CHCl_3$,
0° to rt, 24 h



I +



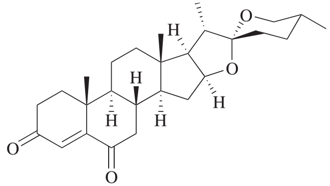
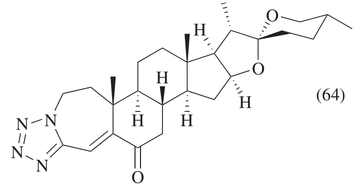
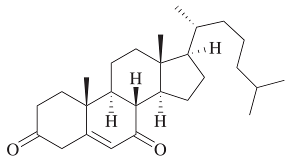
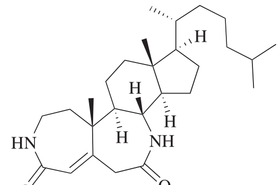
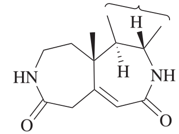
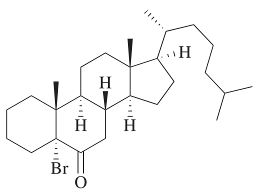
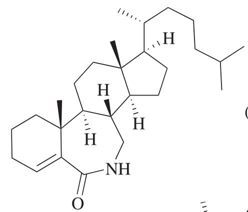
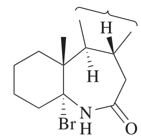
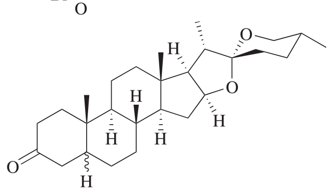
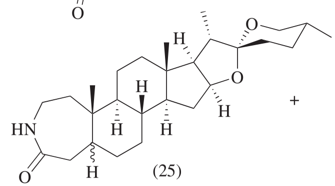
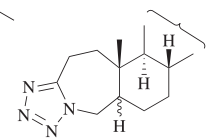
II +



III

I + **II** + **III** (20), **I**:**II**:**III** = 3:2:1 535

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27} 	HN_3, BF_3•OEt_2, $CHCl_3$, 0° to rt, 24 h	 (64)	526
	NaN_3, PPA, 60°, 10 h	 **I** ; **I** or **II** (40)[e] ;  **II**	536
	HN_3, BF_3•OEt_2, $CHCl_3$, 0° to rt, 24 h	**I** or **II** (18)[e]	536
	NaN_3, H_2SO_4, PhH, rt, 1 h	 (—) +  (—)	537
	HN_3, 70°	 (25) +  (23)	538

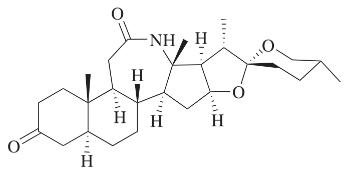
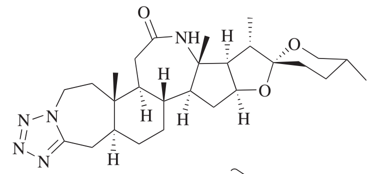
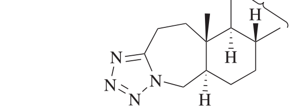
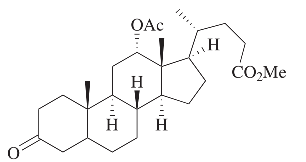
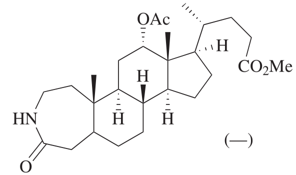
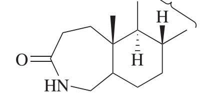
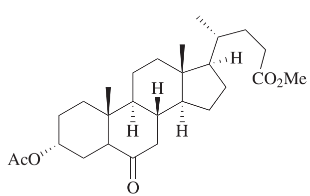
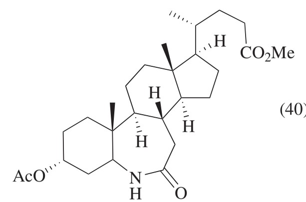
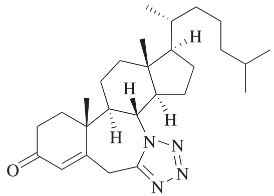
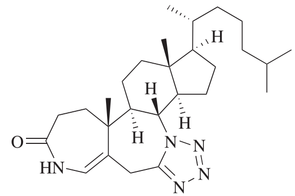
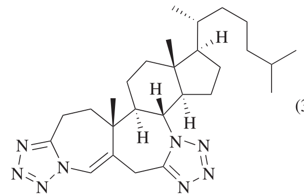
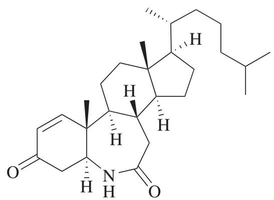
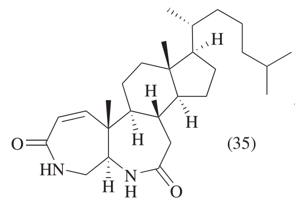
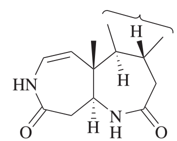
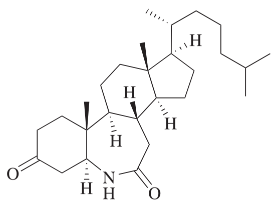
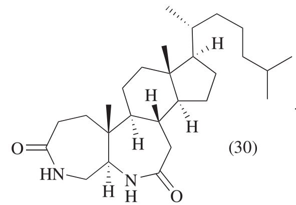
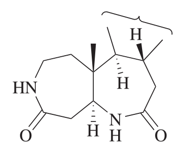
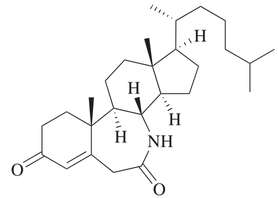
	HN_3, $BF_3•OEt_2$, $CHCl_3$, 0° to rt, 24 h	 (13) +  (13)	535
	HN_3, PPA	 (—) +  (—)	539[d]
	HN_3, H_2SO_4, PhH	 (40)	539[d]

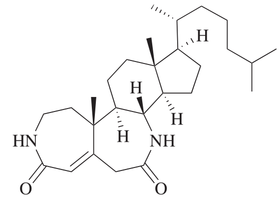
TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27} 	NaN_3, PPA, 50°, 10 h	 (39)	540
	HN_3, BF_3•OEt_2, $CHCl_3$, 0° to rt, 28 h	 (32)	540
	NaN_3, H_2SO_4, $CHCl_3$, rt, 1 h	 (35) +  (10)	541
	NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 1.5 h	 (30) +  (35)	541

C_{27-29}

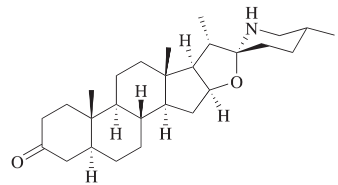


NaN_3, PPA, 60°, 12 h

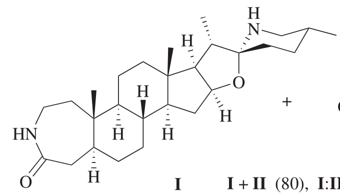


(13)

542

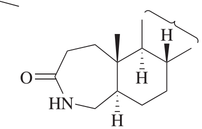


NaN_3, CCl_3CO_2H[b]



I

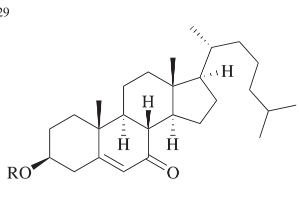
+



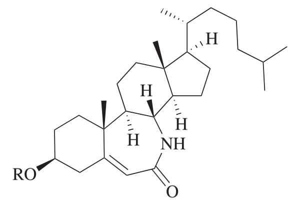
II

I + **II** (80), **I**:**II** = 3:1

543

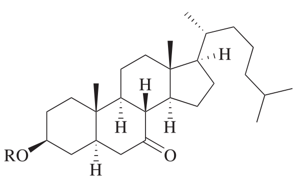


HN_3, H_2SO_4, PhH, 0°, 2 h

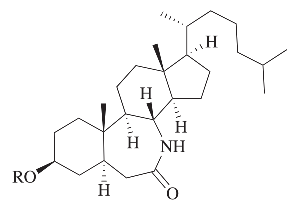


R	
H	(—)
Ac	(—)

544



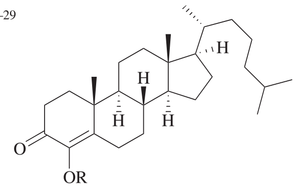
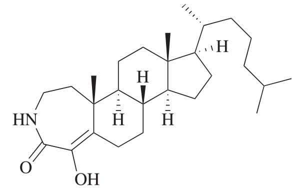
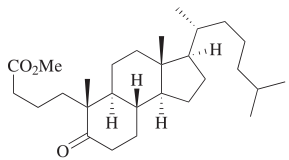
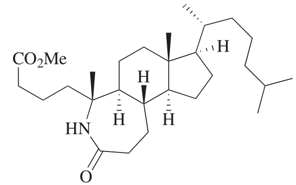
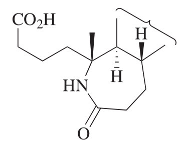
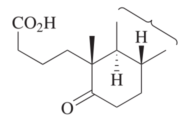
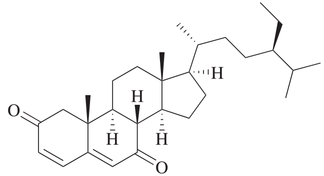
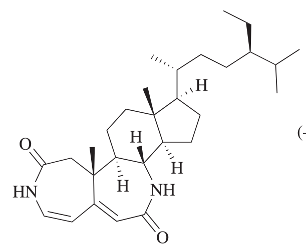
HN_3, H_2SO_4, PhH, 0°, 2 h



R	
H	(—)
Ac	(—)

544
545

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27-29} 	NaN_3, PPA, 50°, 6 h	 R: H (58); Ac (58)	528
C_{28} 	NaN_3, PPA, 60°, 10 h	 (30) +  (17) +  (8)	546
	NaN_3, H_2SO_4	 (—)	547

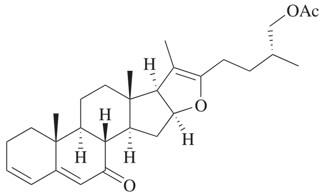
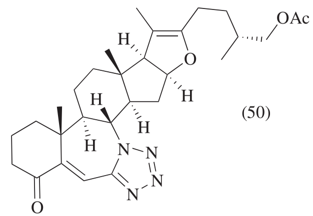
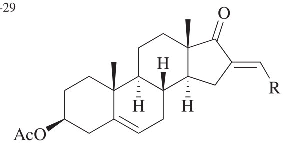
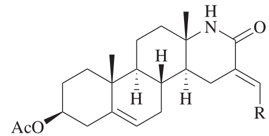
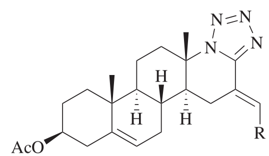
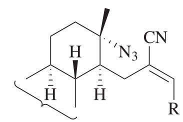
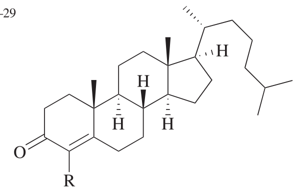
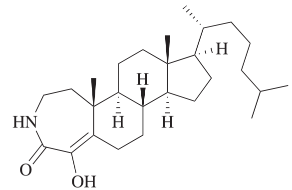
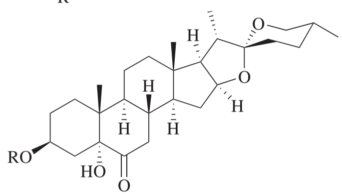
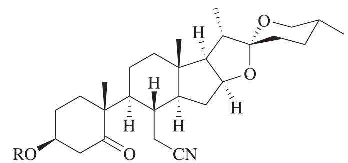
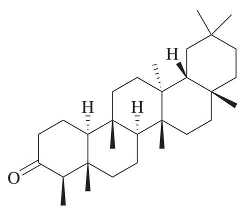
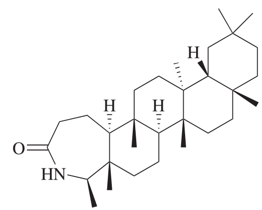
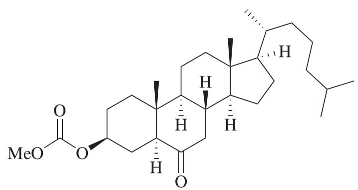
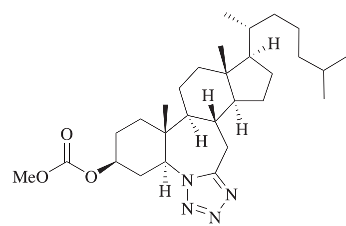
C_{28-29} 	HN_3, BF_3•OEt_2, PhH, rt, 80 h	 (50)	548
	NaN_3, H_2SO_4, PhH, rt, 1 h	 (—) R: Ph, 4-HOC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$	549
	HN_3, BF_3•OEt_2, PhH, 0° to rt, 24 h	 **I** +  **II** **I** + **II** (—) R: Ph, 4-HOC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$	549

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28-29}			
	HN_3, BF_3•OEt_2, PhH, rt, 3 d	 R: MeO (60); AcO (50)	530
	NaN_3, H_2SO_4, PhH	 R: Me (—); Et (—)	550
C_{29}			
	HN_3, H_2SO_4, $CHCl_3$, 0°, 2 h	 (64)	551
	HN_3, BF_3•OEt_2, PhH, 0° to rt, 35 h	 (—)	552

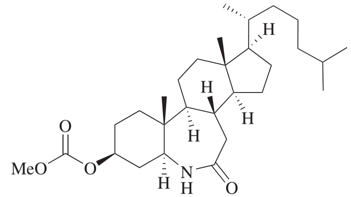
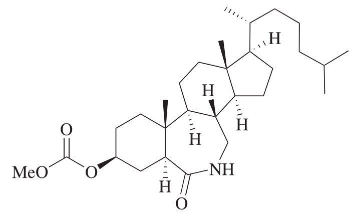
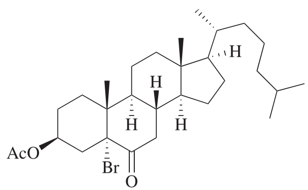
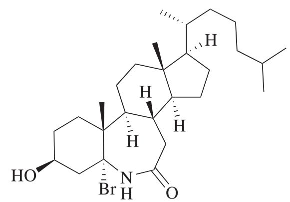
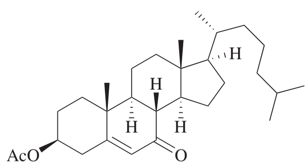
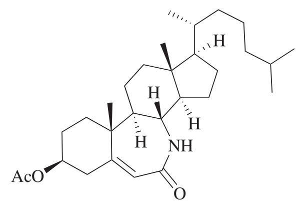
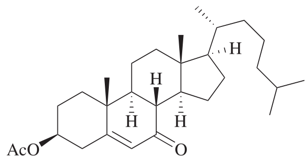
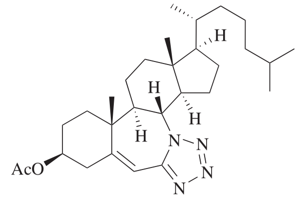
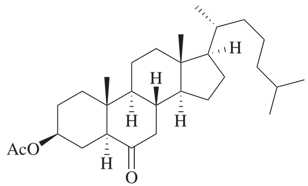
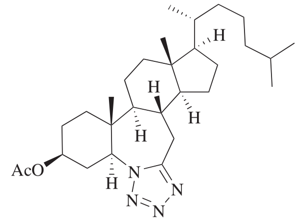
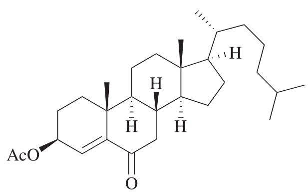
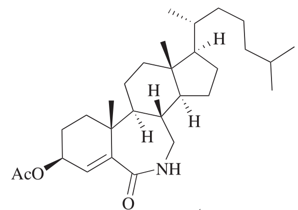
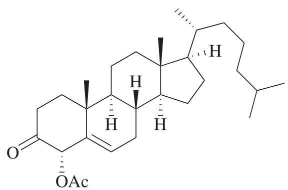
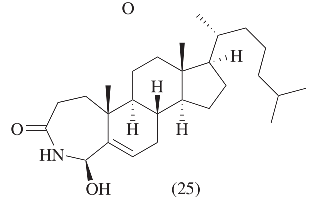
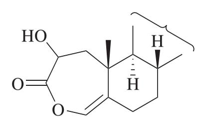
	NaN_3, H_2SO_4, PhH	 (—) +  (—)	552
	NaN_3, H_2SO_4, PhH, rt, 1 h	 (36)	537
	NaN_3, H_2SO_4, PhH, rt, 30 min	 (50)	553

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29}			
	HN_3, BF_3•OEt_2, PhH, 0° to rt, 5 h	 (—)	553
	HN_3, BF_3•OEt_2, PhH, 0° to rt, 35 h	 (—)	554
	NaN_3, PPA, 60°, 8 h	 (15)	531
	HN_3, BF_3•OEt_2, PhH, rt, 24 h	 (25) +  (20)	532

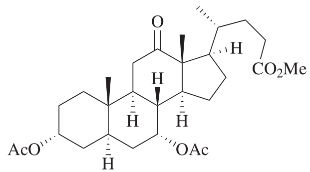
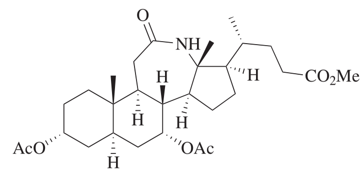
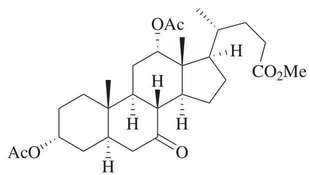
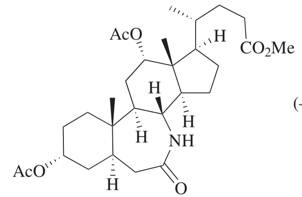
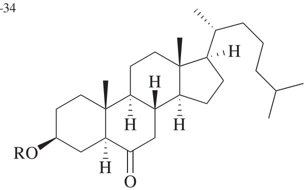
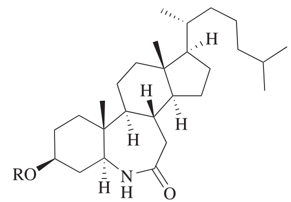
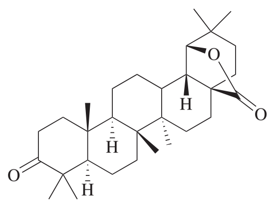
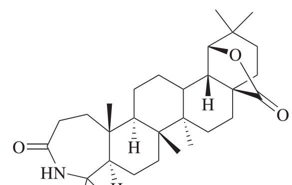
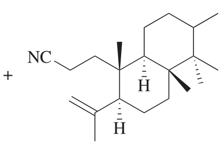
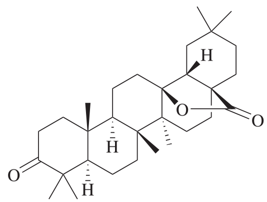
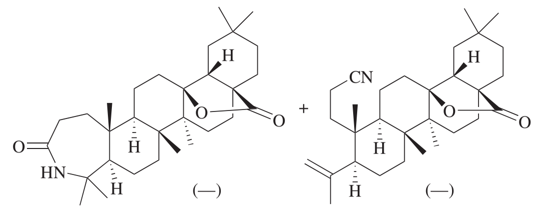
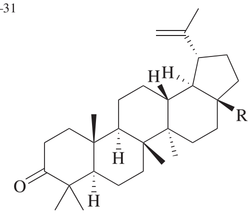
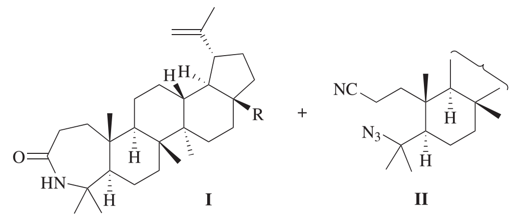
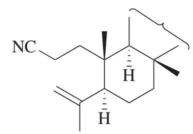
	HN_3, H_2SO_4, PhH, rt, 1 h	 (—)	539
	HN_3, PPA	 (—)	539
C_{29-34}			
	NaN_3, PPA, 100°, 10 h	 R: Ac (73); Bz (22)	544
C_{30}			
	NaN_3, PPA, 60°, 10 h	 (—) +  (—)	555[d]

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30} 	NaN_3, PPA, 60°, 10 h	 (—) + (—)	555
$C_{30–31}$ 	A: HN_3, BF_3•OEt_2, PhH, rt, 16 h B: HN_3, H_2SO_4, PhH, rt, 16 h	 **I** + **II**	556
		R / Conditions / **I** / **II**: Me / A / (—) / (45) Me / B / (57) / (—) MeO_2C / A / (—) / (45) MeO_2C / B / (57) / (—)	
	NaN_3, H_2SO_4, AcOH, 30–70°, 12 h	**I** +  **III**	557, 555
		R / **I + III**: Me / (—) MeO_2C / (—)	

C$_{31}$

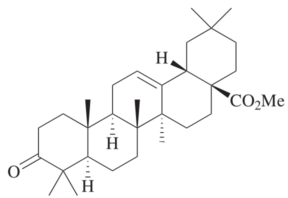
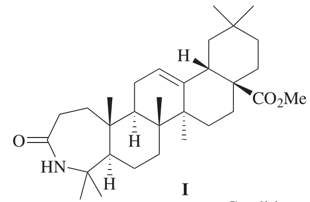
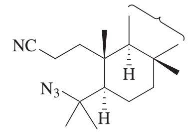
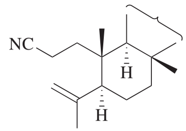
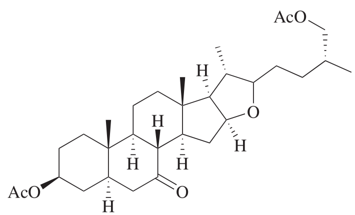
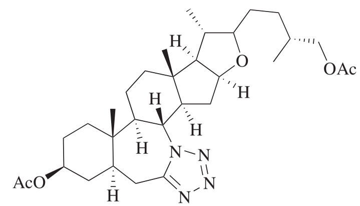
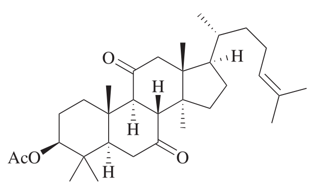
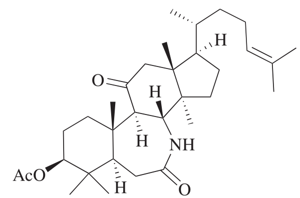
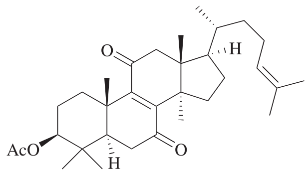
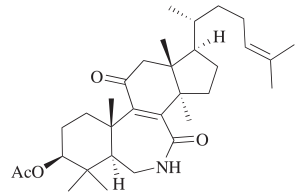
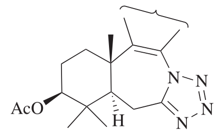
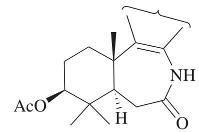
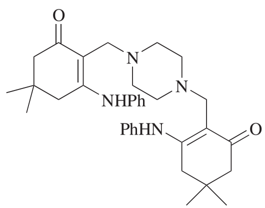
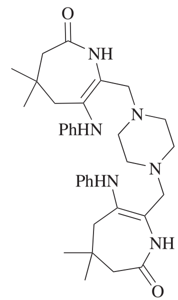
	A: HN_3, BF_3•OEt_2, PhH, rt, 16 h B: HN_3, H_2SO_4, PhH, rt, 16 h	 **I** +  **II** Conditions / I / II A / (—) / (45) B / (57) / (—)	556
	NaN_3, H_2SO_4, AcOH, 30–70°, 12 h	**I** (—) +  (—)	557
	HN_3, BF_3•OEt_2, PhH, rt, 80 h	 (—)	548[d]
	NaN_3, H_2SO_4, 0°, 15 min	 (44)	558

TABLE 4. SCHMIDT REACTIONS OF CARBOCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{31} 	NaN_3, H_2SO_4, 0°, 30 min	 (50) +  (—) +  (—)	558
C_{34} 	NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 5 h	 (70)	478

[a] Silica sulfuric acid is silica-bound sulfuric acid generated by treating silica with chlorosulfonic acid.

[b] Molten trichloroacetic acid (mp 57°) was used as solvent.

[c] The structure was initially assigned incorrectly. It has been corrected here, see reference 401.

[d] The stereochemistry of the substrate was not specified in the reference.

[e] A single isomer of unassigned structure was obtained.

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3

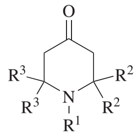
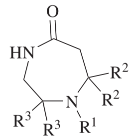
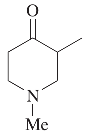
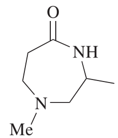
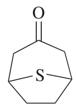
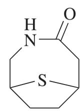
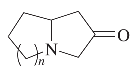
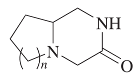
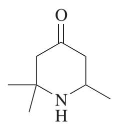
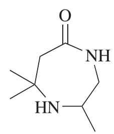
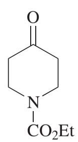
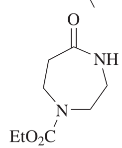
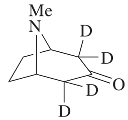
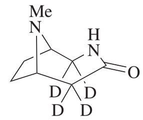
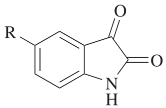
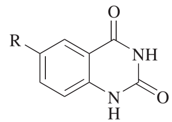
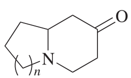
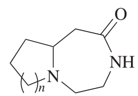
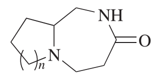
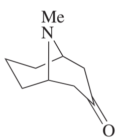
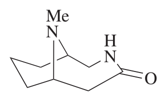
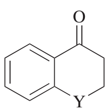
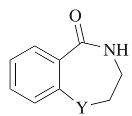
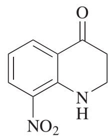
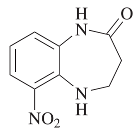
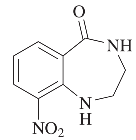
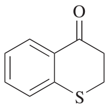
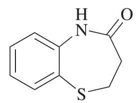
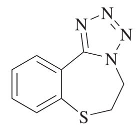
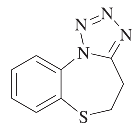
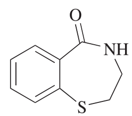
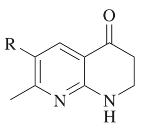
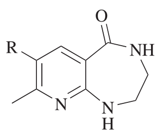
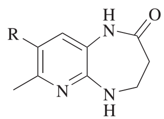
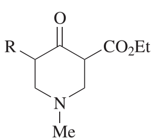
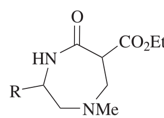
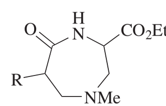
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-9} 	NaN_3, H_2SO_4, $CHCl_3$, 0°, 45 min	 R^1 R^2 R^3: H H H (88); Me H H (53); H Me Me (51)	559
C_7 	NaN_3, H_2SO_4, 0°, 1 h	 (38)	57
	HN_3, P_2O_5, H_2SO_4, $CHCl_3$, 30°, 6 h	 (73)	560
C_{7-8} 	NaN_3, H_2SO_4, $CHCl_3$, 0–50°, 2 h	 *n*: 1 (44); 2 (65)	561
C_8 	NaN_3, H_2SO_4, 0°, 1 h	 (64)	57
	NaN_3, H_2SO_4, 0°, 3 h	 (70)	562

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		NaN_3, D_2SO_4, 0–50°, 3 h	 (89)	563
C_{8-9}		$TMSN_3$, $FeCl_3$, DCE, rt, 30–35 min	 **I** R: H (80); Me (75)	286
		NaN_3, $FeCl_3$, DCE, rt, 2.5 h	**I** R: H (74); Me (75)	286
		NaN_3, H_2SO_4, $CHCl_3$, 0–50°, 2 h	 **I** +  **II** *n* = 1: **I** (22), **II** (0) *n* = 2: **I** (20), **II** (—)	561
C_9		NaN_3, H_2SO_4, $CHCl_3$, 0–50°, 4 h	 (90)	564
		HN_3, P_2O_5, $CHCl_3$, 20°, 4 h	 Y: O (67); S (68)	560

	NaN_3, MsOH	 (10) +  (86)	565
	$TMSN_3$, TFA, rt, 72 h	 **I** (—) +  (30) +  (—)	566
	NaN_3, H_2SO_4, PhH, 0° to rt, 12 h	**I** (80) +  (—)	567
	NaN_3, H_2SO_4, $CHCl_3$, rt, 1 h	 **I** +  **II**	65
C_{9-10}			
	HN_3, H_2SO_4, $CHCl_3$, 0°, 3 h	 **I** +  **II**	568

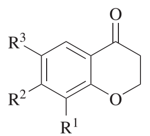
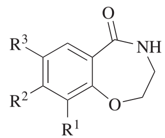
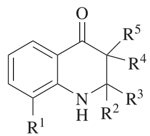
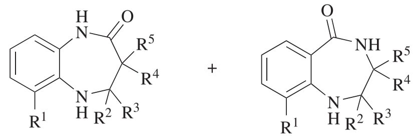
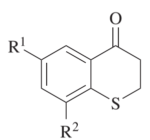
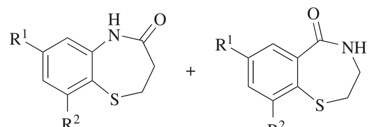
Yields for reference 65:

R	**I**	**II**
H	(2)	(79)
Br	(12)	(73)

Yields for reference 568:

R	**I**	**II**
H	(—)	(30)
Me	(—)	(30)

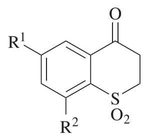
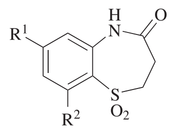
TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10} 	NaN_3, H_2SO_4, 0° to rt, 12 h		62
C_{9-11} 	NaN_3, H_2SO_4, rt, 2 h	 **I** + **II**	569
	NaN_3, H_2SO_4	 **I** + **II**	570

R^1	R^2	R^3	
H	H	H	(78)
H	H	Cl	(65)
H	H	Br	(70)
Cl	H	H	(75)
H	H	Me	(79)
Me	H	H	(70)
H	MeO	H	(50)
H	H	MeO	(52)

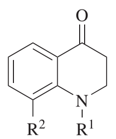
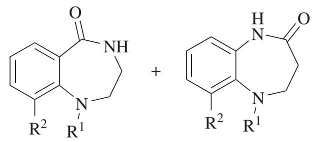
R^1	R^2	R^3	R^4	R^5	**I**	**II**
H	H	H	H	H	(30)	(0)
Me	H	H	H	H	(52)	(0)
H	H	H	Me	H	(45)	(27)
H	Me	Me	H	H	(77)	(0)
H	H	H	Me	Me	(0)	(79)

R^1	R^2	**I**	**II**
H	H	(42)	(21)
Cl	H	(78)	(0)
Br	H	(84)	(0)
Me	H	(36)	(44)
Me	Me	(21)	(33)

	NaN_3, H_2SO_4			570

R^1	R^2	
H	H	(67)
Cl	H	(52)
Br	H	(15)
Me	H	(79)
Me	Me	(15)

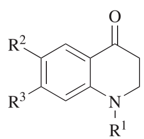
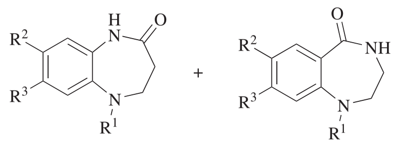
C_{9-12}

	NaN_3, MsOH			

I **II**

R^1	R^2	**I**	**II**	
H	HO	(49)	(22)	571
H	O_2N	(86)	(10)	565
H	MeO	(70)	(18)	571
Ac	MeO	(90)	(0)	571

C_{9-15}

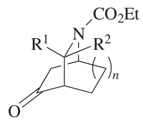
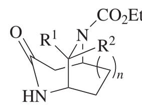
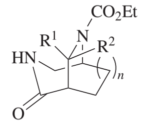
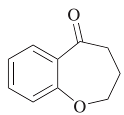
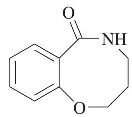
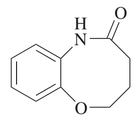
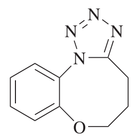
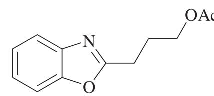
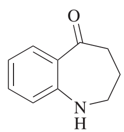
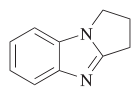
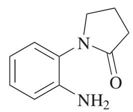
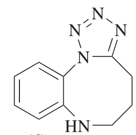
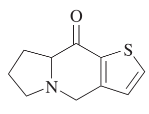
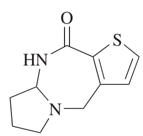
	NaN_3, H_2SO_4, $CHCl_3$, rt, 2 h		572

I **II**

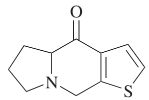
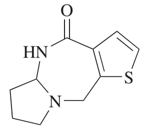
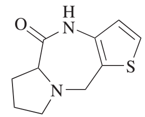
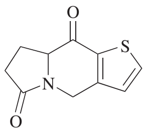
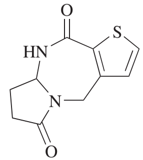
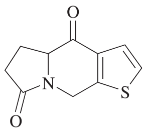
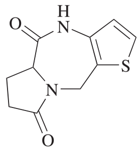
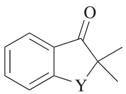
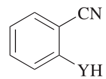
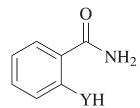
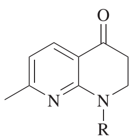
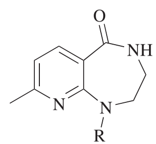
R^1	R^2	R^3	**I + II**	**I:II**
H	H	H	(88)	1:4
H	Cl	H	(92)	1:2
H	H	MeO	(95)	3:7
Me	H	H	(82)	1:3
Me	Cl	H	(91)	1:3

R^1	R^2	R^3	**I + II**	**I:II**
Me	H	MeO	(92)	1:2
Ac	H	H	(85)	19:1
Ac	Cl	H	(80)	9:1
Ac	H	MeO	(90)	9:1
Ph	H	H	(82)	1:3

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-16} 	NaN_3, H_2SO_4, rt, 1–3 h	 **I** +  **II**	67
C_{10} 	NaN_3, H_2SO_4, AcOH, 60°, 6 h	 (5) +  (54) +  (4) +  (13)	573
	NaN_3, H_2SO_4, AcOH, 0° to rt, 24 h	 (65) +  (8) +  (6)	573
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (85)	574

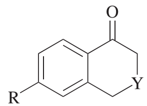
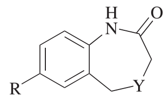
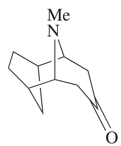
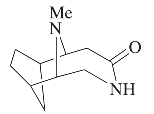
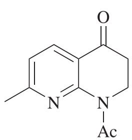
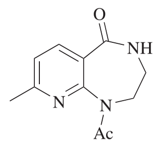
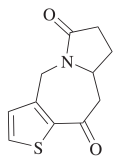
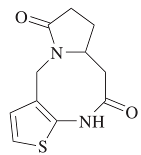
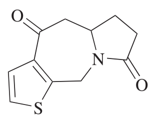
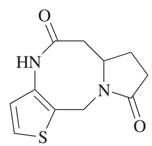
n	R^1	R^2	**I + II**	**I:II**
0	H	H	(38)	100:0
1	H	H	(62)	73:27
1	Me	H	(43)	70:30
1	H	Me	(72)	55:45
2	H	H	(82)	67:33
1	Ph	H	(50)	73:27
1	H	Ph	(97)	35:65

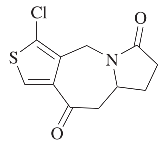
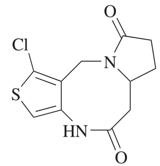
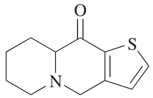
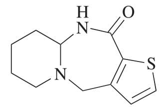
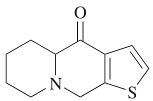
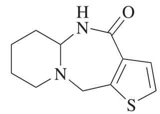
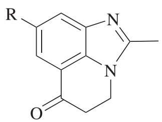
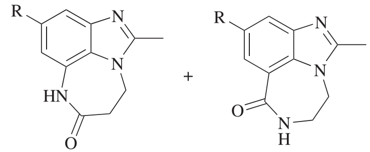
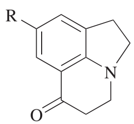
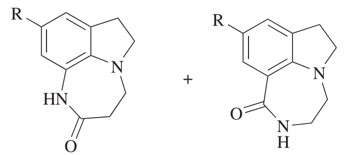
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (59) +  (32)	574
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 48 h	 (70)	574
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 12 h	 (75)	574
	NaN_3, H_2SO_4, AcOH, 0° to rt, 24 h	 **I** +  **II**	573
C_{10-11}			
	NaN_3, H_2SO_4, $CHCl_3$		65

Y	**I**	**II**
HN	(88)	(6)
O	(51)	(29)

R	
Me	(78)
Et	(79)

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

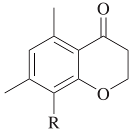
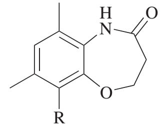
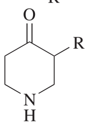
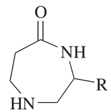
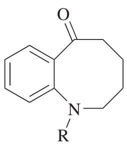
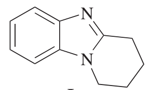
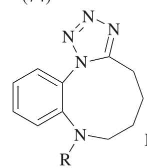
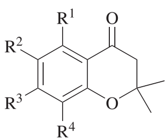
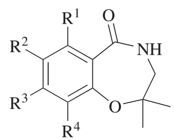
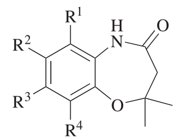
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-14} 	NaN_3, H_2SO_4, PhH, 0° to rt, 12 h	 R / Y: MeO / S (—); H / EtN (—); MeO / EtN (63)	575
C_{11} 	NaN_3, H_2SO_4	 (93)	576
	NaN_3, H_2SO_4, $CHCl_3$, rt, 1 h	 (69)	65
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 24 h	 (65)	66
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 24 h	 (70)	66

	NaN_3, H_2SO_4, CH_2Cl_2, rt, 24 h	 (45)	66
	NaN_3, H_2SO_4, CH_2Cl_2, 0° to rt, 6 h	 (—)	577
	NaN_3, H_2SO_4, CH_2Cl_2, 0° to rt, 6 h	 (—)	577
	NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 16 h	 **I** + **II**	578
	NaN_3, PPA, 60°, 4 h	 **I** + **II**	579

R	**I**	**II**
H	(46)	(50)
Cl	(14)	(78)
O_2N	(0)	(70)

R	**I + II**	**I:II**
H	(74)	1:5
Cl	(68)	1:11

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12} 	NaN_3, H_2SO_4, rt, 16 h		62
C_{11-13} 	HN_3, H_2SO_4, $CHCl_3$, 0°, 1.5 h		568
C_{11-18} 	NaN_3, H_2SO_4, AcOH, 0° to rt, 24 h	 **I** +  **II**	573
C_{11-27} 	NaN_3, H_2SO_4, AcOH, 50°, 3 h	 **I** +  **II**	580

C_{11-12}:

R	
H	(5)
Me	(5)

C_{11-13}:

R	
Ph	(71)
Bn	(74)
$BnCH_2$	(74)

C_{11-18}:

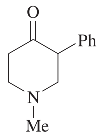
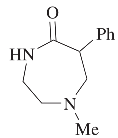
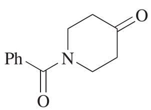
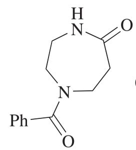
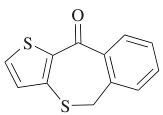
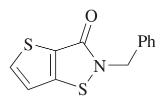
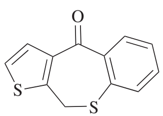
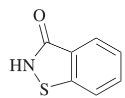
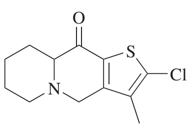
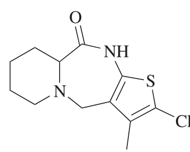
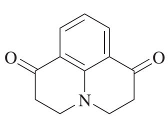
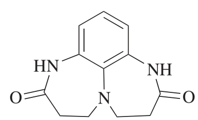
R	**I**	**II**
H	(54)	(23)
Ac	(50)	(20)
Ts	(50)	(20)

C_{11-27}:

R^1	R^2	R^3	R^4	**I**	**II**
H	H	H	H	(57)	(0)
H	H	MeO	H	(47)	(0)
H	H	MsO	H	(53)	(0)
H	H	MeO	Me	(55)	(0)
Me	H	MeO	H	(0)	(49)
H	MeO	MeO	H	(54)	(0)
MeO	H	MeO	H	(0)	(54)

H	H	$NCCH_2O$	H	(45)	(0)
H	H	HO_2CCH_2O	H	(64)	(0)
H	H	H_2NCOCH_2O	H	(51)	(0)
Me	H	MsO	H	(0)	(47)
H	H	HO_2CCH_2O	Me	(75)	(0)
H	H	EtO_2CCH_2O	H	(71)	(0)
H	H	EtO_2CCH_2O	Me	(73)	(0)
H	H	$PhSO_3$	H	(35)	(0)
H	H	BnO	H	(71)	(0)
H	HO	BnO	H	(42)	(0)
H	H	$2\text{-}ClC_6H_4CH_2O$	H	(52)	(0)
H	H	$4\text{-}ClC_6H_4CH_2O$	H	(61)	(0)
H	H	PNBO	H	(91)	(0)
H	H	$4\text{-}BrC_6H_4CH_2O$	H	(48)	(0)
H	H	TsO	H	(47)	(0)
Me	H	BnO	H	(0)	(59)
Me	H	$2\text{-}ClC_6H_4CH_2O$	H	(0)	(58)
Me	H	PNBO	H	(0)	(46)
Me	H	$4\text{-}BrC_6H_4CH_2O$	H	(0)	(44)
H	H	$PhNHCOCH_2O$	H	(46)	(0)
H	H	$2\text{-}ClC_6H_4NHCOCH_2O$	H	(61)	(0)
H	H	$3\text{-}ClC_6H_4NHCOCH_2O$	H	(87)	(0)
H	H	$2\text{-}BrC_6H_4NHCOCH_2O$	H	(62)	(0)
H	H	$3\text{-}BrC_6H_4NHCOCH_2O$	H	(61)	(0)
H	H	$2,6\text{-}Cl_2C_6H_3NHCOCH_2O$	H	(48)	(0)
Me	H	$PhNHCOCH_2O$	H	(0)	(57)
H	H	$PhNHCOCH_2O$	Me	(62)	(0)
H	H	$2\text{-}MeC_6H_4NHCOCH_2O$	H	(54)	(0)
H	H	$2\text{-}Me\text{-}6\text{-}EtC_6H_3NHCOCH_2O$	H	(52)	(0)
H	$PhSO_2O$	$PhSO_2O$	H	(42)	(0)
H	TsO	TsO	H	(45)	(0)
H	$4\text{-}MeC_6H_4COHNCH_2O$	BnO	H	(39)	(0)

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	NaN_3, H_2SO_4, $CHCl_3$, 10°, 30 min	 (41)	581
	HN_3, P_2O_5, H_2SO_4, CH_2Cl_2, 20°, 4 h	 (72)	560
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 3 h	 (47)	582
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 3 h	 (35)	582
	NaN_3, H_2SO_4, CH_2Cl_2, 0° to rt, 6 h	 (—)	169
	NaN_3, H_2SO_4, $CHCl_3$, 0°, 15 min	 (81)	583

C$_{12-13}$

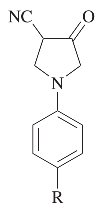
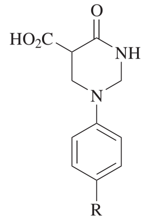
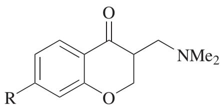
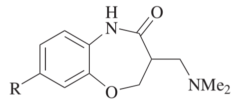
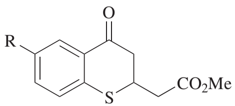
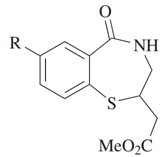
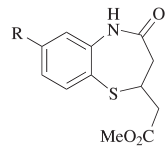
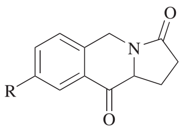
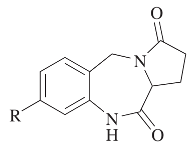
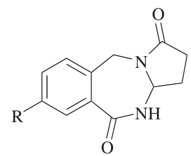
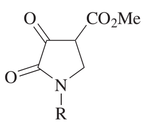
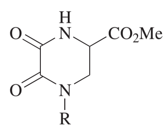
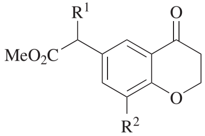
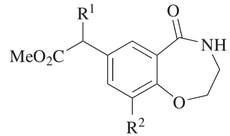
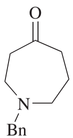
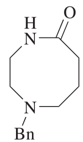
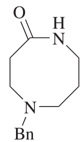
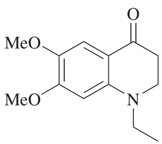
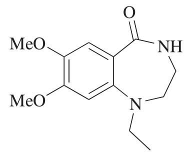
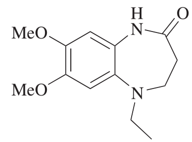
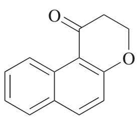
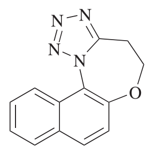
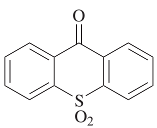
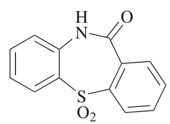
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3, $CHCl_3$, concd H_2SO_4	 R: Me (82); MeO (84)	584
	NaN_3, H_2SO_4, rt, 16 h	 R: H (70); MeO (—)	62
	NaN_3, H_2SO_4, PhH, 0° to rt, 12 h	 **I** +  **II**; R, **I**, **II**: H (36) (24); Cl (—) (—); Me (30) (44)	585
	NaN_3, H_2SO_4, CH_2Cl_2, 0°, 3 h	 **I** +  **II**; R, **I**, **II**: H (100) (0); F (60) (40); Me (72) (28)	169
	NaN_3, H_2SO_4	 R: Ph (75); Bn (70)	322

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-14} 	NaN_3, H_2SO_4, PhH, rt, 12 h	 R^1 / R^2: H / H (52); H / HO (15); H / Cl (34); Me / H (57); Et / H (46)	586
C_{13} 	NaN_3, H_2SO_4, rt to 50°, 37 h	 (64) +  (—)	55
	NaN_3, H_2SO_4, $CHCl_3$	 (28) +  (54)	587
	NaN_3, $SiCl_4$, MeCN, rt, 12 h	 (40)	70
	NaN_3, CCl_3CO_2H, $CHCl_3$, rt, 12 h	 (100)	588

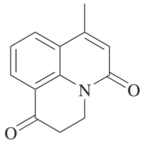
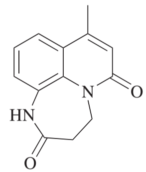
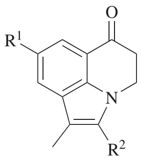
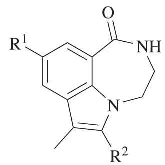
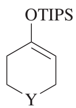
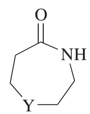
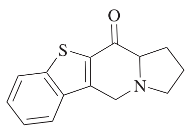
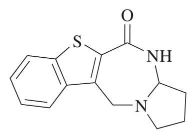
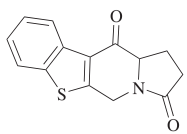
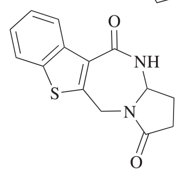
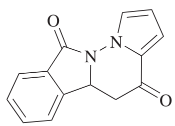
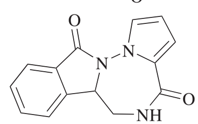
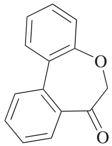
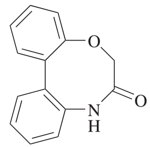
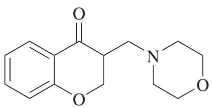
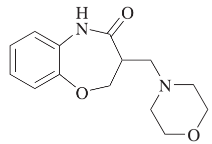
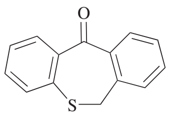
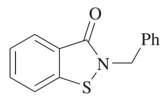
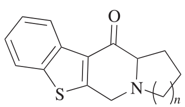
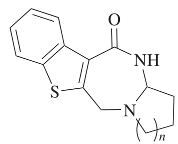
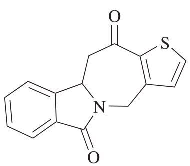
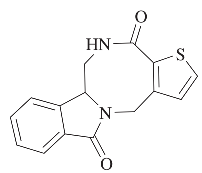
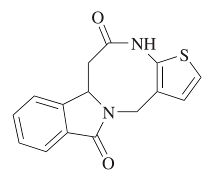
		NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 5 h	 (59)	589
C_{13-14}		NaN_3, CCl_3CO_2H,[a] 60°	 R^1 R^2 Cl Me (—) H Et (—)	590
C_{14}		1. $TMSN_3$, PPTS, CH_2Cl_2, rt, 2 d 2. $h\nu$, c-C_6H_{12}, 0°, 1 h	 Y O (76) S (62)	74
		NaN_3, H_2SO_4, CH_2Cl_2, rt, 72 h	 (80)	591
		NaN_3, H_2SO_4, CH_2Cl_2, rt, 72 h	 (51)	591
		NaN_3, H_2SO_4, CH_2Cl_2, 0° to rt, 12 h	 (68)	592

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	NaN_3, H_2SO_4, 0° to rt, 2 h	 **I** (58)	593
	NaN_3, PPA, 50°, 4 h	**I** (38)	593
	NaN_3, H_2SO_4, rt, 16 h	 (20)	62
	NaN_3, H_2SO_4, CH_2Cl_2, rt, 3 h	 (51)	582
C_{14-15} 	NaN_3, H_2SO_4, CH_2Cl_2, rt, 72 h	 *n* 1 (65); 2 (51)	591
C_{15} 	NaN_3, H_2SO_4	 (32) +  (42)	594

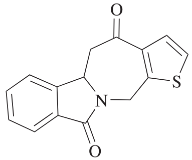
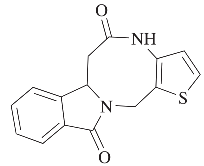
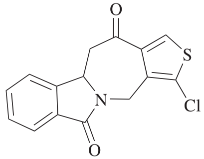
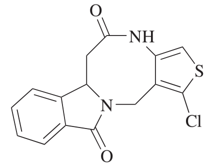
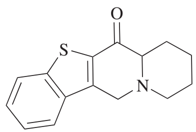
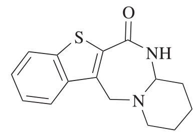
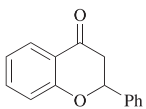
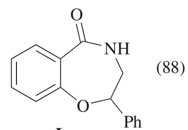
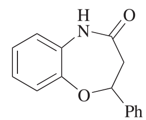
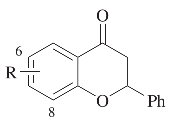
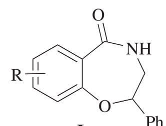
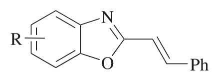
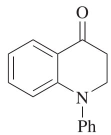
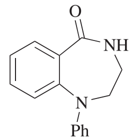
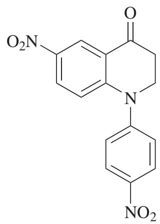
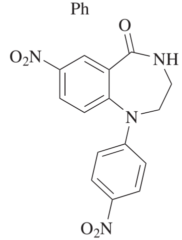
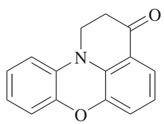
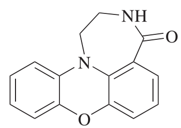
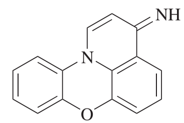
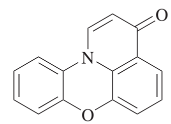
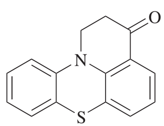
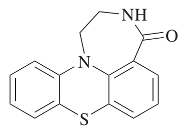
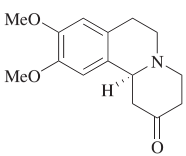
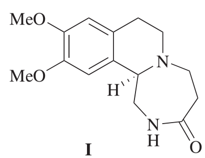
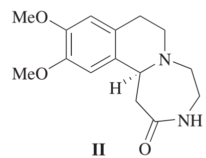
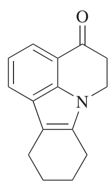
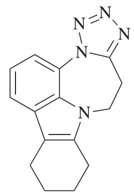
	NaN_3, H_2SO_4	 (81)	594
	NaN_3, H_2SO_4	 (76)	594
	NaN_3, H_2SO_4, CH_2Cl_2, 0° to rt, 6 h	 (—)	577
	NaN_3, H_2SO_4, AcOH, 0° to rt, 24 h	 **I** (88) +  (3)	595
	Azide, $FeCl_3$, DCE, rt	**I** Azide / Time $TMSN_3$ 50 min (75) NaN_3 3 h (68)	286
	NaN_3, H_2SO_4, AcOH, 40°	 **I** +  **II** R / I / II 6-O_2N (70) (5) 8-O_2N (70) (—)	596

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h	 (—)	597
		NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h	 (69)	597
		NaN_3, CCl_3CO_2H,[a] $CHCl_3$, 70°, 5 h	 (20) +  (13) +  (6)	598
		NaN_3, CCl_3CO_2H,[a] 60°, 5 h	 (—)	599
		NaN_3, H_2SO_4, CH_2Cl_2, rt, 4 h	 **I** +  **II** **I** + **II** (90)	600

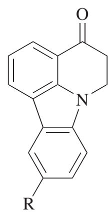


NaN$_3$, SiCl$_4$, MeCN, rt, 6 h

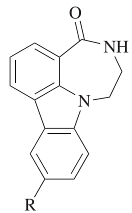


(90)

70

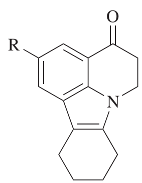


NaN$_3$, CCl$_3$CO$_2$H,[a] 60°

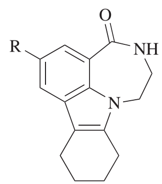


R	
H	(—)
Cl	(—)

590



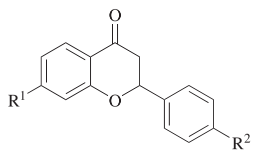
NaN$_3$, CCl$_3$CO$_2$H,[a] 60°



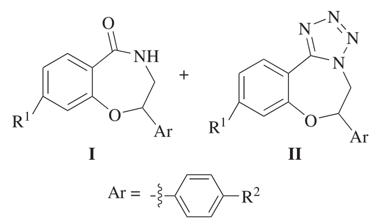
R	
H	(—)
Cl	(—)

590

C_{15-16}

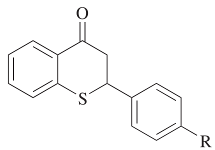
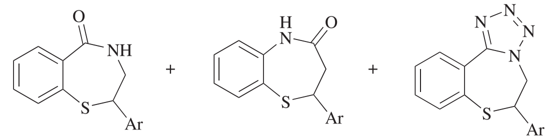
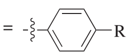
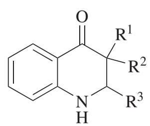
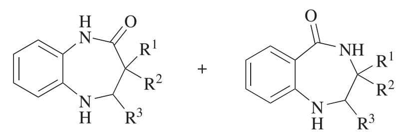


TMSN$_3$, TFA



R^1	R^2	**I**	**II**	
H	H	(25)	(3)	600a
H	F	(—)	(—)	600b
F	H	(—)	(28)	600a
H	Cl	(—)	(10)	600a
Cl	H	(—)	(6)	600a
H	O_2N	(—)	(—)	600b
H	Br	(—)	(10)	600a
Br	H	(—)	(7)	600a
MeO	H	(—)	(—)	600b

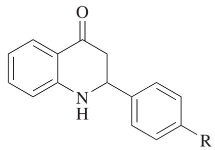
TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15-16} 	$TMSN_3$, TFA, rt, 72 h	 I + II + III; Ar = 	566
C_{15-17} 	NaN_3, H_2SO_4, rt, 2 h	 I + II	601

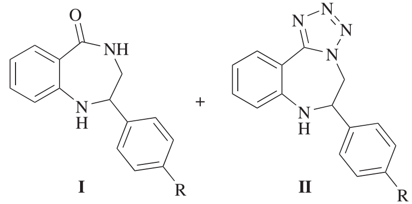
R	I	II	III
H	(40)	(20)	(22)
F	(35)	(—)	(—)
Cl	(33)	(—)	(—)
Br	(28)	(—)	(—)
MeO	(—)	(—)	(—)

R^1	R^2	R^3	I	II
H	H	Ph	(81)	(0)
H	H	$4\text{-}ClC_6H_4$	(79)	(0)
Me	H	Ph	(0)	(73)
Me	Me	Ph	(0)	(84)
Et	H	Ph	(0)	(76)

C_{15-21}



A: NaN_3, H_2SO_4, AcOH, 50°, 4 h
B: $TMSN_3$, TFA, rt, 5 d
C: NaN_3, $SnCl_4$, CH_2Cl_2, rt, 5 d
D: NaN_3, TFA, rt, 5 d



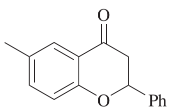
I + **II**

R	Conditions	**I**	**II**
H	A	(35)	(30)
H	B	(28)	(30)
H	C	(5)	(60)
H	D	(5)	(38)
Me	A	(40)	(38)
Me	B	(35)	(35)

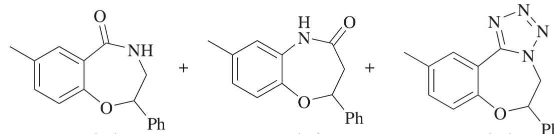
R	Conditions	**I**	**II**
Me	C	(4)	(65)
Me	D	(5)	(40)
Ph	A	(30)	(30)
Ph	B	(35)	(30)
Ph	C	(5)	(62)
Ph	D	(5)	(40)

73

C_{16}

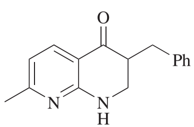


NaN_3, AcOH, 40°

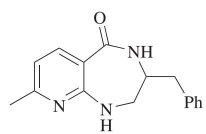


(—) + (—) + (—)

596



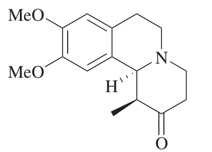
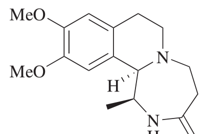
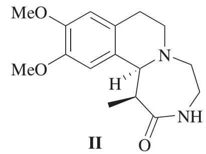
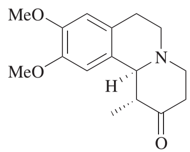
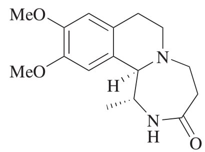
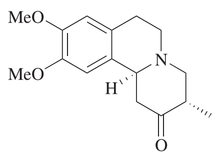
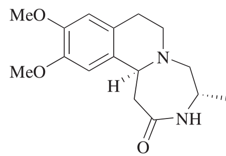
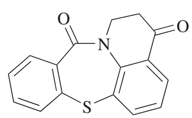
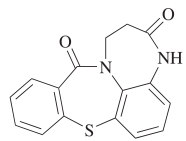
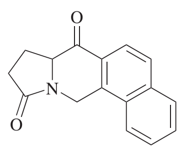
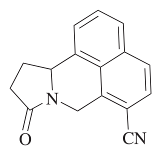
NaN_3, H_2SO_4, $CHCl_3$



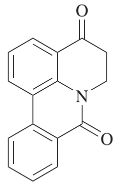
(64)

602

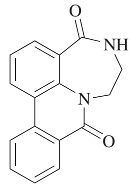
TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}		NaN_3, H_2SO_4, CH_2Cl_2, rt, 4 h	 **I** +  **II** **I + II** (69), **I**:**II** = —	600
		NaN_3, H_2SO_4, CH_2Cl_2, rt, 4 h	 (67)	600
		NaN_3, H_2SO_4, CH_2Cl_2, rt, 4 h	 (82)	600
		A: NaN_3, H_3PO_4, 65°, 5 h B: NaN_3, CCl_3CO_2H,[a] 80°, 20 h C: NaN_3, PPA, 65°, 5 h D: NaN_3, H_2SO_4, rt, 3 h	 Conditions: A (77); B (60); C (39); D (28)	603
		NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 3 h	 (32)	604

C$_{16-17}$

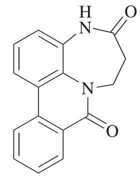


NaN_3, CCl_3CO_2H,[a] 60°



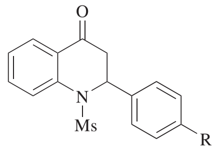
(—)

+

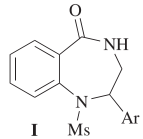


(—)

590

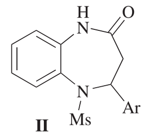


$TMSN_3$, TFA, rt, 72 h



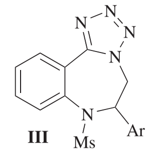
I

+



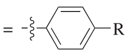
II

+



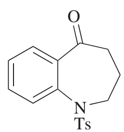
III

605

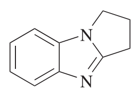
Ar = 

R	**I**	**II**	**III**
H	(35)	(25)	(20)
F	(30)	(10)	(20)
Cl	(35)	(20)	(30)
Br	(40)	(25)	(20)
MeO	(0)	(30)	(35)

C$_{17}$

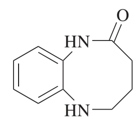


NaN_3, H_2SO_4, rt, 2.5 h



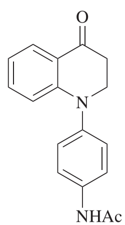
(41)

+

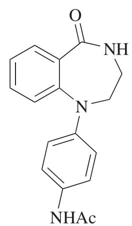


(—)

606



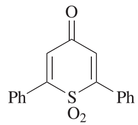
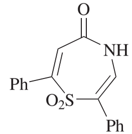
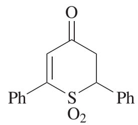
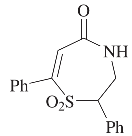
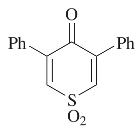
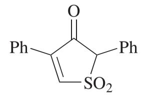
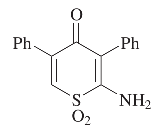
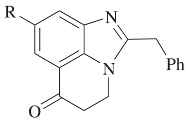
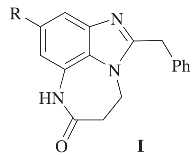
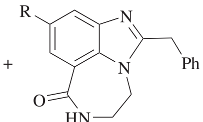
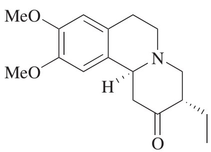
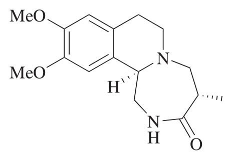
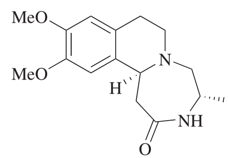
NaN_3, H_2SO_4, $CHCl_3$, rt, 3 h

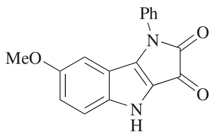
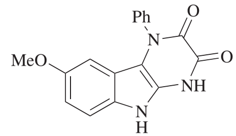
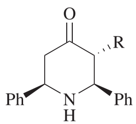
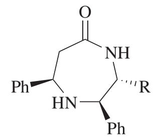
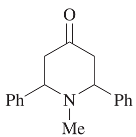
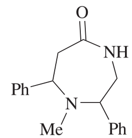
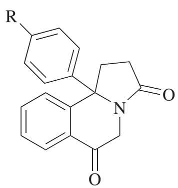
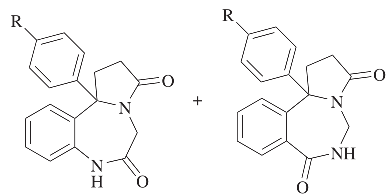


(74)

597

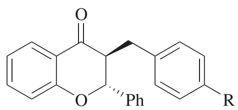
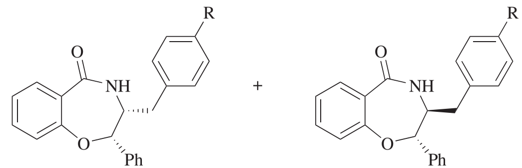
TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	NaN_3, H_2SO_4, 0° to rt	 (58)	607
	NaN_3, H_2SO_4, 0° to rt	 (64)	607
	NaN_3, H_2SO_4, 0° to rt	 (30) +  (3)	607
	NaN_3, H_2SO_4, $CHCl_3$, 0° to rt, 16 h	 **I** +  **II** R / **I** / **II** Cl / (10) / (76) O_2N / (1) / (74)	578
	NaN_3, H_2SO_4, $CHCl_3$, 0°	 (2) +  (90)	608

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3, H_2SO_4, $CHCl_3$	 (65)	322
$C_{17–20}$ 	NaN_3, H_2SO_4, $CHCl_3$, rt, 1.5 h	 (—) R: H, Me, Et, *i*-Pr	609
C_{18} 	HN_3, H_2SO_4, $CHCl_3$, 0°, 1.5 h	 (95)	568
	NaN_3, H_2SO_4, $CHCl_3$, 50°, 1.5 h	 **I** + **II**	610

R	**I**	**II**
H	(41)	(4)
Cl	(55)	(4)

TABLE 5. SCHMIDT REACTIONS OF HETEROCYCLIC KETONES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22-23} 	NaN_3, $AcOH/H_2SO_4$ (5:1), 55°, 12 h	 **I** + **II**	611

R	**I + II**	**I:II**
H	(80)	9:1
Cl	(72)	1:0
MeO	(63)	9:1

[a] Molten trichloroacetic acid (mp 57°) was used as solvent.

TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN_3

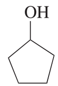
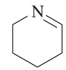
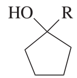
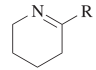
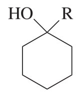
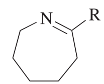
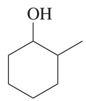
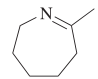
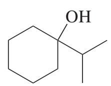
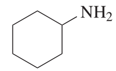
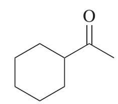
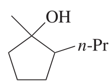
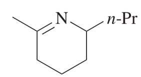
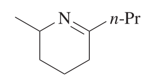
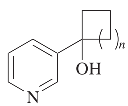
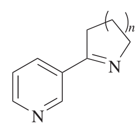
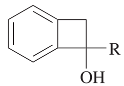
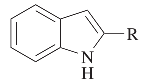
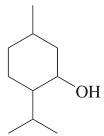
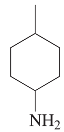
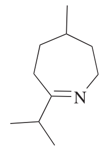
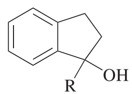
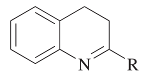
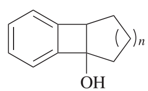
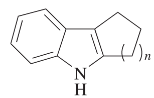
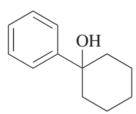
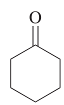
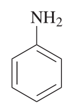
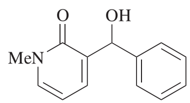
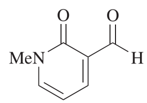
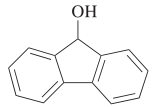
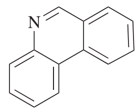
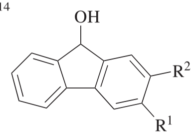
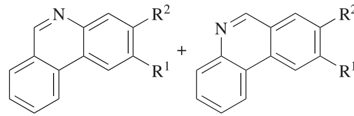
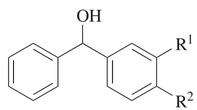
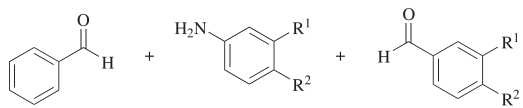
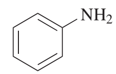
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	HN_3, H_2SO_4, $CHCl_3$, rt, 2 h	 (60)	612
$C_{6–9}$ 	1. HN_3, BF_3•OEt_2 2. H_2SO_4, $CHCl_3$	 R: Me (—); *n*-Pr (93); *n*-Bu (—)	39
$C_{6–12}$ 	NaN_3, H_2SO_4, rt, 2 h	 R: H (—)	613
		Me (22)	614
		Et (—)	614
		c-C_6H_{11} (—)	614
C_7 	HN_3, H_2SO_4, $CHCl_3$, rt, 2 h	 (30)	612
C_9 	NaN_3, H_2SO_4, rt, 2 h	 (—) +  (6)	614
	1. HN_3, BF_3•OEt_2 2. H_2SO_4, $CHCl_3$	 (—) +  (—)	39
$C_{9–10}$ 	HN_3, H_2SO_4, CH_2Cl_2	 *n*: 1 (65); 2 (75)	615

TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN_3 (*Continued*)

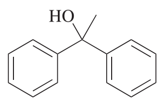
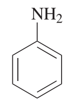
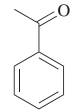
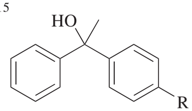
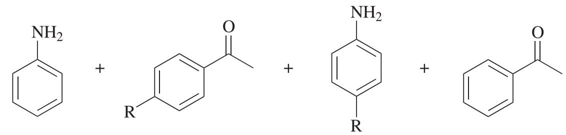
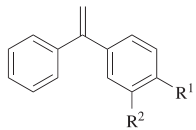
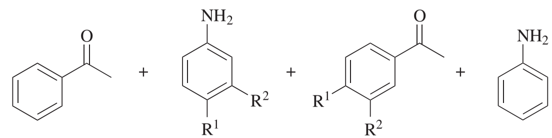
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-15} 	1. HN_3, BF_3•OEt_2, PhH 2. H_2SO_4, $CHCl_3$, 0°	 R / Me (90) / allyl (95) / Ph (95) / Bn (85)	616
C_{10} 	HN_3, H_2SO_4, $CHCl_3$, rt, 2 h	 (14) +  (7)	612
C_{10-16} 	HN_3, H_2SO_4, PhH	 R / Me (35) / Bn (30)	41
C_{11-12} 	1. HN_3, BF_3•OEt_2, PhH, 0°, 10 min 2. H_2SO_4, PhH	 **I** *n* / 1 (85) / 2 (90)	616
	HN_3, H_2SO_4, PhH	**I** *n* / 1 (85) / 2 (90)	616
C_{12} 	NaN_3, H_2SO_4, rt, 2 h	 (42) +  (71)	614

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	NaN_3, H_2SO_4, $CHCl_3$	 (70)	329
	NaN_3, H_2SO_4, $CHCl_3$, 0–50°, 12 h	 (—)	617
C_{13-14} 	NaN_3, H_2SO_4, $CHCl_3$, rt, 12 h	 **I** + **II**	170
	1. HN_3, Cl_3CCO_2H, $CHCl_3$ 2. concd H_2SO_4, 0–55°	 **I** + **II** (—) + **III**  **IV** (—)	

R^1	R^2	**I**	**II**
O_2N	H	(2)	(90)
H	O_2N	(5)	(83)
H_2N	H	(0)	(33)
MeO	H	(11)	(21)
H	MeO	(—)	(—)
Me	H	(40)	(40)
H	Me	(54)	(14)

R^1	R^2	**I + III**[a]	**I**:**III**	Refs.
H	H	(—)	—	617
H	Cl	(41)	1.0:1.3	618
Cl	H	(53)	1.0:3.7	618
H	Br	(73)	1.7:1.0	618
H	Me	(80)	3.4:1.0	618
H	MeO	(46)	6.3:1.0	618

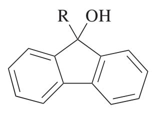
TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	NaN_3, H_2SO_4, rt	 (65) +  (40)	619
C_{14-15} 	HN_3, CCl_3CO_2H, PhH	 **I** + **II** (—) + **III** + **IV** (—)	620
C_{14-16} 	NaN_3, H_2SO_4, $CHCl_3$, 0° to rt	 **I** + **II** (—) + **III** + **IV** (—)	

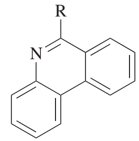
R	I + III[b]	I:III
Cl	(25)	3:1
Br	(48)	3:1
Me	(43)	1:4
MeO	(37)	0:1

R^1	R^2	I	III	Refs.
F	H	(46)	(26)	621
Br	H	(16)	(30)	621
H	Me	(34)	(15)	621
Me	Me	(37)	(7)	621
Et	H	(45)	(10)	621
EtO	H	(—)[c]	(—)[c]	42

C_{14-17}

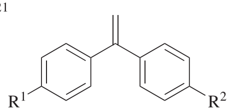


NaN_3, H_2SO_4, $CHCl_3$, rt, 1.5 h

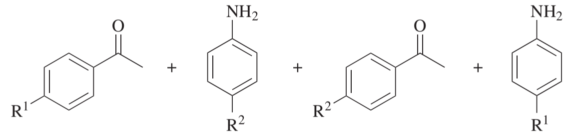


R		Refs.
Me	(47)	170
Et	(87)	622
i-Pr	(85)	622
t-Bu	(64)	622

C_{14-21}



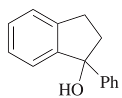
NaN_3, H_2SO_4, $CHCl_3$, 0° to rt



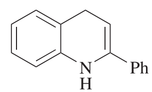
I + **II** (—) + **III** + **IV** (—) 623

R^1	R^2	**I**	**III**
H	H	(55)	(—)
H	Cl	(18)	(29)
H	MeO	(49)	(8)
H	Me	(40)	(8)
MeO	Me	(8)	(39)
H	Ph	(39)	(17)
MeO	Ph	(11)	(36)
Me	Ph	(6)	(21)

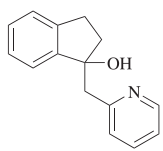
C_{15}



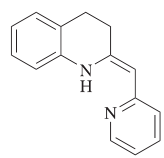
HN_3, H_2SO_4, $CHCl_3$, rt, 2 h



(91) 41

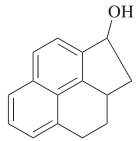
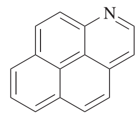
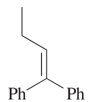
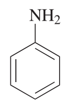
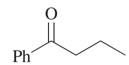
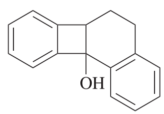
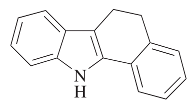
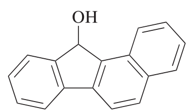
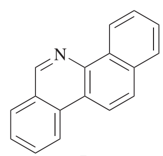
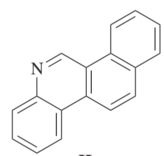
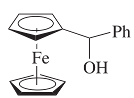
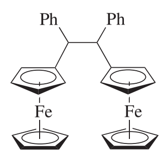
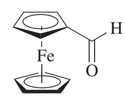
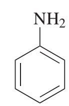


HN_3, H_2SO_4, $CHCl_3$, rt, 2 h



(93) 41

TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	1. NaN_3, MsOH, rt, 18 h 2. 10% Pd/C	 (—)	624
C_{16} 	NaN_3, H_2SO_4, rt	 (57) +  (64)	619
	1. HN_3, BF_3•OEt_2, PhH 2. H_2SO_4, PhH	 **I** (92)	616
	HN_3, H_2SO_4, PhH	**I** (92)	616
C_{17} 	1. NaN_3, CCl_3CO_2H, $CHCl_3$, rt, 2 h 2. H_2SO_4, $CHCl_3$	 **I** +  **II** **I** + **II** (—), **I**:**II** = 2.9:1	388
	1. HN_3, CCl_3CO_2H, PhH 2. AcOH, rt, 18 h	 (—) +  (—) +  (—)	625

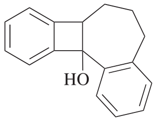
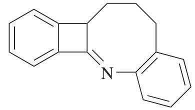
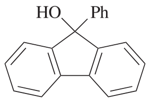
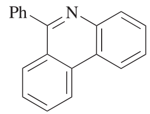
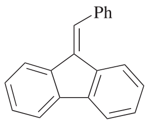
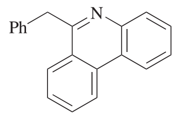
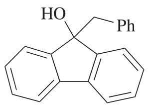
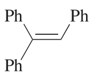
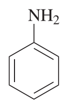
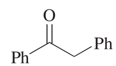
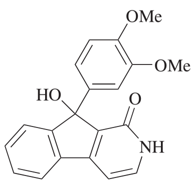
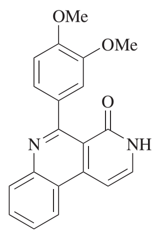
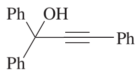
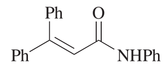
		1. HN_3, BF_3•OEt_2, PhH 2. H_2SO_4, $CHCl_3$	 (96)	616
C_{19}		NaN_3, H_2SO_4, $CHCl_3$, rt, 1.5 h	 (94)	170
C_{20}		NaN_3, H_2SO_4, $CHCl_3$, rt, 1.5 h	 (49) **I**	170
		NaN_3, H_2SO_4, $CHCl_3$, rt, 1.5 h	**I** (40)	170
		NaN_3, H_2SO_4, rt	 (30) +  (25)	619
		NaN_3, PPA, 25–45°, 12 h	 (87)	329

TABLE 6. SCHMIDT REACTIONS OF ALCOHOLS AND ALKENES WITH HN_3 (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	HN_3, H_2SO_4, $CHCl_3$, 0°, 1.5 h	 (15)	353

[a] The products were isolated as mixtures of the corresponding carboxylic acids after oxidation.

[b] The products were isolated as mixtures of the corresponding amine hydrochlorides.

[c] The ratio of **I**:**III** was 6.2:1.

TABLE 7. SCHMIDT REACTIONS OF NITRO COMPOUNDS WITH HN_3

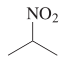
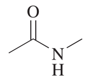
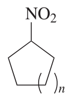
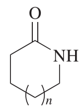
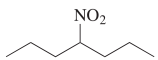
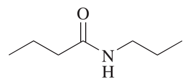
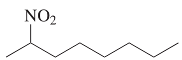
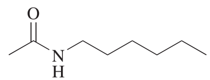
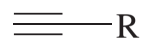
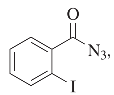
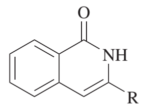
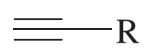
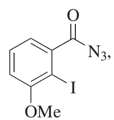
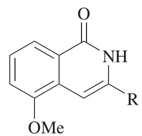
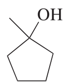
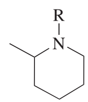
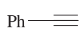
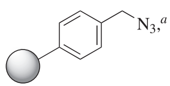
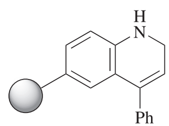
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	1. NaN_3, NaOH, H_2O, heat 2. H_2SO_4, $CHCl_3$, rt	 (44)	84
$C_{5–6}$ 	1. NaN_3, NaOH, H_2O, heat 2. H_2SO_4, $CHCl_3$, rt	 *n*: 1 (67); 2 (81)	84
C_7 	1. NaN_3, NaOH, H_2O, heat 2. H_2SO_4, $CHCl_3$, rt	 (62)	84
C_8 	1. NaN_3, NaOH, H_2O, reflux 2. H_2SO_4, $CHCl_3$, rt	 (47)	84

TABLE 8. SCHMIDT REACTIONS OF CARBOCATIONS WITH ALKYL AND ACYL AZIDES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-8} 	 Pd/C, PPh_3, CuI, Et_3N, EtOH, 80°, 12 h	 R: $HO(CH_2)_2$ (82); $HOCMe_2$ (82); $HO(CH_2)_3$ (85); $MeCH(OH)CH_2$ (60); $Cl(CH_2)_3$ (56); $HO(CH_2)_4$ (55); $NC(CH_2)_3$ (73); n-C_6H_{13} (44)	626
C_{4-9} 	 Pd/C, PPh_3, CuI, Et_3N, EtOH, 80°, 12 h	 R: $HO(CH_2)_2$ (78); $HO(CH_2)_3$ (84); $NC(CH_2)_3$ (65); n-C_6H_{13} (85); Ph (43); 4-MeC_6H_4 (40)	626
C_6 	1. RN_3, TfOH, CH_2Cl_2 2. $NaBH_4$, MeOH	 R: n-Bu (95); Bn (86)	24
C_8 	 TfOH, CH_2Cl_2, 0° to rt	 (>95)	627

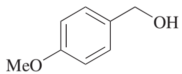
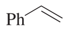
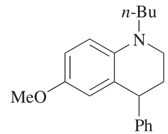
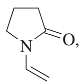
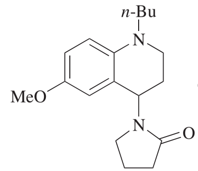
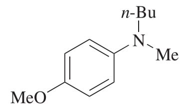
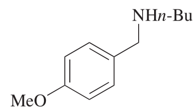
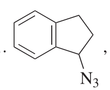
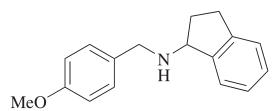
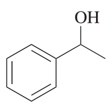
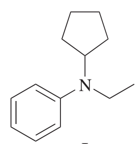
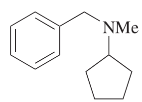
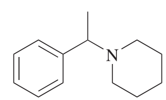
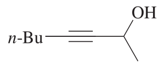
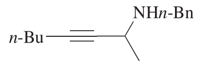
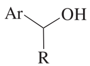
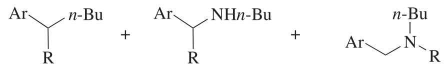
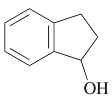
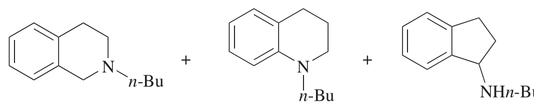
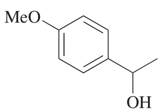
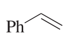
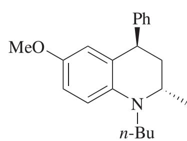
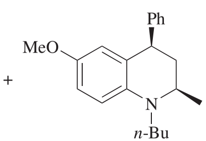
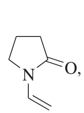
	, n-BuN_3, TfOH, CH_2Cl_2, rt, 12 h	 (66)	628
	 n-BuN_3, TfOH, CH_2Cl_2, rt, 12 h	 (77)	628
	1. n-BuN_3, $SnCl_4$, CH_2Cl_2 2. $NaBH_4$, MeOH	 **I** +  **II** **I** + **II** (97), **I**:**II** = 1:2	17
	1. , $SnCl_4$, CH_2Cl_2 2. $NaBH_4$, MeOH	 (69)	17
	1. c-$C_5H_9N_3$, $SnCl_4$, CH_2Cl_2 2. $NaBH_4$, MeOH	 **I** +  **II** +  **III** **I** + **II** + **III** (57), **I**:**II**:**III** = 2.5:1:2	24

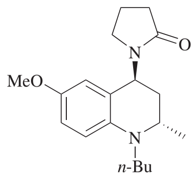
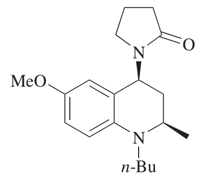
TABLE 8. SCHMIDT REACTIONS OF CARBOCATIONS WITH ALKYL AND ACYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	1. n-BuN_3, TfOH, CH_2Cl_2 2. $NaBH_4$, MeOH	 (48)	24
C_{8-13} 	1. n-BuN_3, $SnCl_4$ or TfOH, CH_2Cl_2 2. $NaBH_4$, MeOH	 **I** + **II** + **III**	24
C_9 	1. n-BuN_3, TfOH, PhH 2. $NaBH_4$	 **I** + **II** + **III** **I + II + III** (73), **I:II:III** = 28:8:1	24
	, n-BuN_3, $SnCl_4$, PhH, reflux, 12 h	 (10) +  (39)	628

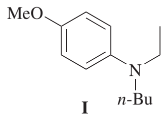
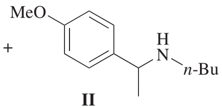
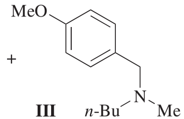
Aryl	R	**I + II + III**	**I:II:III**
Ph	Me	(81)	4.5:1:1
4-MeC_6H_4	H	(61)	1:6:0
4-$MeOC_6H_4$	H	(97)	1:2:0
$3,4$-$(OCH_2O)C_6H_3$	H	(100)	1:2:0
$3,4$-$(MeO)_2C_6H_3$	H	(98)	1:1.5:0
4-$MeOC_6H_4$	Me	(97)	12.5:2.5:1
4-$MeOC_6H_4$	*i*-Pr	(91)	3.5:0:1
4-PhC_6H_4	H	(77)	1:3:0



n-BuN$_3$, TfOH, CH_2Cl_2, rt, 12 h

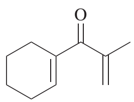

(9) +

(27) 628

1. n-BuN$_3$, $SnCl_4$, CH_2Cl_2
2. $NaBH_4$, MeOH

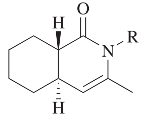
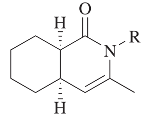

I +

II +

III 17

I + II + III (95), **I:II:III** = 12:2.5:1

C_{10}



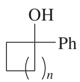
RN_3, BF_3•OEt_2, $NaHCO_3$, CH_2Cl_2, 0°, 0.5 h


I +

II

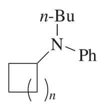
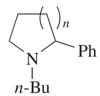
R	**I + II**	**I:II**
Bn	(80)	2:1
Ph(CH$_2$)$_3$	(70)	3:1
(*E*)-PhCH=CHCH$_2$	(73)	2.5:1

629

C_{10-12}



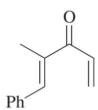
1. n-BuN$_3$, TfOH, CH_2Cl_2
2. $NaBH_4$, MeOH


I +

II

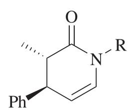
n	**I + II**	**I:II**
1	(97)	1:5.1
2	(66)	1.1:1
3	(82)	2.4:1

24

C_{12}



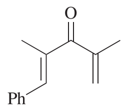
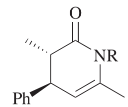
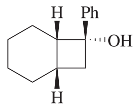
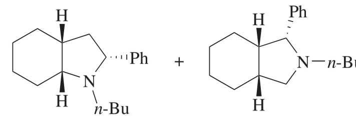
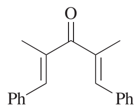
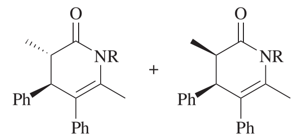
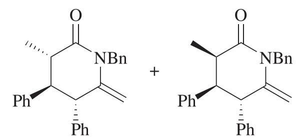
RN_3, BF_3•OEt_2, $NaHCO_3$, CH_2Cl_2, 0°, 1 h



R	
Bn	(62)
Ph(CH$_2$)$_3$	(40)
(*E*)-PhCH=CHCH$_2$	(43)

629

TABLE 8. SCHMIDT REACTIONS OF CARBOCATIONS WITH ALKYL AND ACYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	RN_3, BF_3•OEt_2, $NaHCO_3$, CH_2Cl_2, –78°, 0.5 h	 R: Bn (75); $Ph(CH_2)_3$ (80); (*E*)-$PhCH{=}CHCH_2$ (72)	629
C_{14} 	1. *n*-BuN_3, $SnCl_4$ or TfOH, CH_2Cl_2 2. $NaBH_4$, MeOH	 **I** + **II** **I** + **II** (91), **I**:**II** = 1:1	24
C_{19} 	RN_3, BF_3•OEt_2, $NaHCO_3$, CH_2Cl_2, –78°, 10 min	 **I** + **II**	629
		R: Bn, **I + II** (82), **I:II** 2:1; $Ph(CH_2)_3$, **I + II** (78), **I:II** 2.3:1; (*E*)-$PhCH{=}CHCH_2$, **I + II** (85), **I:II** 2:1	
	BnN_3, BF_3•OEt_2, CH_2Cl_2, –78°, 30 min; 0°, 15 min	 **I** + **II** **I** + **II** (72), **I**:**II** = 1:1	629

[a] The azide was derived from Merrifield resin.

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES

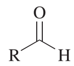
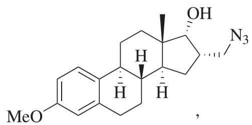
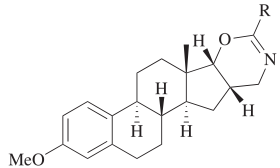
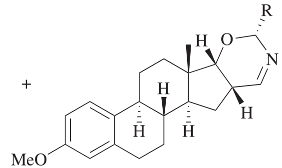
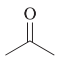
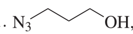
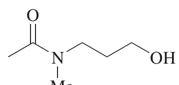
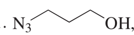
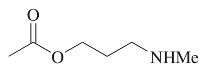
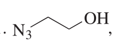
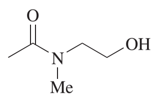
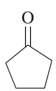
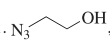
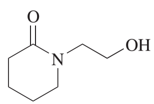
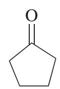
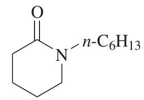
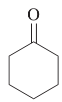
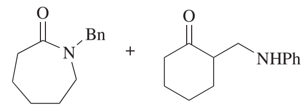
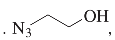
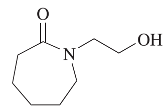
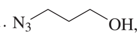
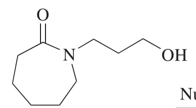
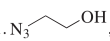
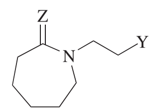
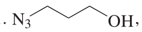
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-7} 	 , BF_3•OEt_2, CH_2Cl_2, 0° to rt, 1 h	 **I** +  **II** R / **I** / **II**: Me (74) (13); Ph (66) (10); 4-$O_2NC_6H_4$ (70) (22)	630
C_3 	1. , BF_3•OEt_2, CH_2Cl_2, rt, 30 min 2. $NaHCO_3$, rt, 30 min	 **I** (86)	95
	1. , BF_3•OEt_2, CH_2Cl_2 2. KOH	**I** (40) +  (19)	48
	1. , BF_3•OEt_2, CH_2Cl_2 2. KOH	 (87)	48
C_5 	1. , BF_3•OEt_2, CH_2Cl_2, rt, 3 h 2. $NaHCO_3$, rt, 30 min	 (96)	95

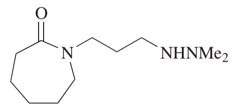
TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	n-$C_6H_{13}N_3$, $TiCl_4$, CH_2Cl_2, rt, 16 h	 (<5)	85
C_6 	BnN_3, Promoter, CH_2Cl_2	 **I** + **II** **I** + **II** (—) (see promoter table below)	85
	1. , BF_3•OEt_2, CH_2Cl_2, rt, 3 h 2. $NaHCO_3$, rt, 30 min	 (98)	95
	1. , BF_3•OEt_2, CH_2Cl_2, rt, 3 h 2. $NaHCO_3$, rt, 30 min	 (90)	95
	1. , BF_3•OEt_2, CH_2Cl_2, rt, 3 h 2. Nucleophile	 (see nucleophile table below)	46

Promoter	**I**:**II**:BnN_3[a]
$TiCl_4$ (1.1 eq)	45:39:16
$TiCl_4$ (2.5 eq)	85:15:0
$SnCl_4$ (1.1 eq)	0:11:89
BF_3•OEt_2 (1.1 eq)	0:11:89
BF_3•OEt_2 (2.5 eq)	0:8:92

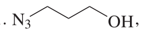
Nucleophile	Y	Z	
NaOH	HO	O	(98)
$Bu_4N^+Ph_3SiF_2^-$	F	O	(64)
Bu_4NI	I	O	(55)
NaN_3	N_3	O	(85)
NaCN	NC–	O	(82)
$NaCH(CO_2Me)_2$	$(MeO_2C)_2CH$	O	(34)
NaOPh	PhO	O	(74)
NaSPh	PhS	O	(95)
$NaCH(SO_2Ph)_2$	$(PhO_2S)_2CH$	O	(54)
$NaCH(CN)_2$	HO	$C(CN)_2$	(71)

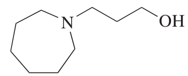
1. ,
BF$_3$•OEt$_2$, CH$_2$Cl$_2$, rt, 3 h
2. Me$_2$NNH$_2$



(88)

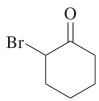
46

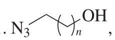
1. ,
BF$_3$•OEt$_2$, CH$_2$Cl$_2$, rt, 3 h
2. NaBH$_4$

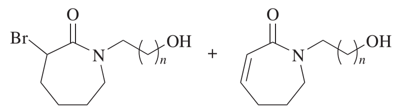


(78)

46

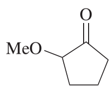


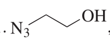
1. ,
BF$_3$•OEt$_2$, CH$_2$Cl$_2$,
0° to reflux, 48 h
2. KOH

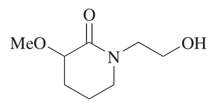


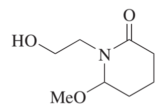
n	**I**	**II**
1	(44)	(14)
2	(42)	(10)

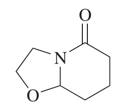
49



1. ,
BF$_3$•OEt$_2$, CH$_2$Cl$_2$,
0° to reflux, 48 h
2. KOH

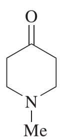


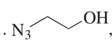
(25)
+


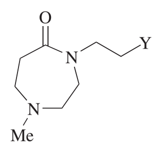
(19)
+


(10)

49



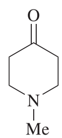
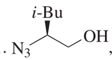
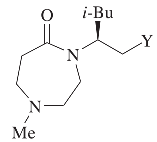
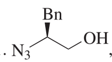
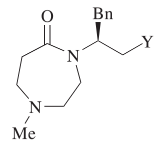
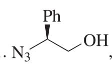
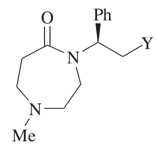
1. ,
BF$_3$•OEt$_2$, CH$_2$Cl$_2$,
0° to rt, 12 h
2. NaY, DMF, 70°, 24 h



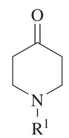
Y	
N_3	(19)
NC–	(37)
PhO	(32)
PhS	(15)
4-BrC$_6$H$_4$S	(62)
4-MeC$_6$H$_4$S	(63)
4-MeOC$_6$H$_4$S	(37)
4-(AcNH)C$_6$H$_4$S	(15)

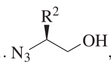
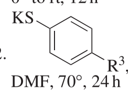
631

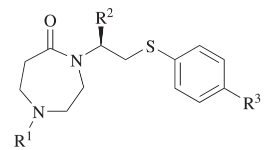
TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
C_6 	1. , BF_3•OEt_2, CH_2Cl_2, 0° to rt, 12 h 2. NaY, DMF, 70°, 24 h		Y		631
			N_3	(8)	
			NC–	(34)	
			PhO	(20)	
			PhS	(7)	
			4-BrC_6H_4S	(20)	
			4-MeC_6H_4S	(58)	
			4-$MeOC_6H_4S$	(34)	
			4-(AcNH)C_6H_4S	(35)	
	1. , BF_3•OEt_2, CH_2Cl_2, 0° to rt, 12 h 2. NaY, DMF, 70°, 24 h		Y		631
			N_3	(63)	
			NC–	(40)	
			PhO	(44)	
			PhS	(18)	
			4-BrC_6H_4S	(44)	
			4-MeC_6H_4S	(62)	
			4-$MeOC_6H_4S$	(40)	
			4-(AcNH)C_6H_4S	(62)	
	1. , BF_3•OEt_2, CH_2Cl_2, 0° to rt, 12 h 2. NaY, DMF, 70°, 24 h		Y		631
			N_3	(58)	
			NC–	(22)	
			PhO	(23)	
			PhS	(8)	
			4-BrC_6H_4S	(22)	
			4-MeC_6H_4S	(16)	
			4-$MeOC_6H_4S$	(20)	
			4-(AcNH)C_6H_4S	(18)	

C6–8



1. ,
BF3•OEt2, CH2Cl2,
0° to rt, 12 h
2. ,
DMF, 70°, 24 h



R^1	R^2	R^3	*b*	*c*
Me	H	Me	(58)	(61)
Me	H	MeO	(55)	(56)
Me	*i*-Bu	Me	(38)	(55)
Me	*i*-Bu	MeO	(85)	(47)
n-Pr	H	Me	(46)	(49)
n-Pr	H	MeO	(57)	(52)
n-Pr	*i*-Bu	Me	(56)	(58)
n-Pr	*i*-Bu	MeO	(47)	(52)

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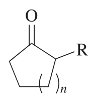
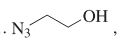
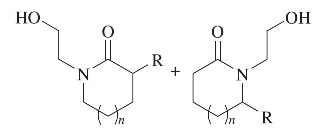
C6–12



1. ,
BF3•OEt2, CH2Cl2, rt, 3 h
2. KOH



I + **II**

R	*n*	**I + II**	**I:II**
Me	1	(89)	53:47
Me	2	(83)	45:55
MeO	2	(52)	91:9
Et	2	(85)	42:58
i-Pr	2	(80)	21:79
t-Bu	2	(11)	13:87
Ph	2	(93)	47:53

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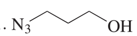
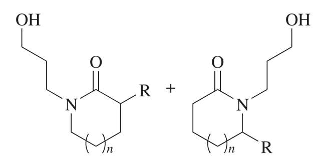
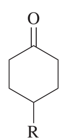
1. ,
BF3•OEt2, CH2Cl2, rt, 3 h
2. KOH



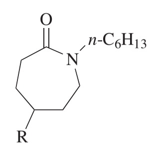
I + **II**

R	*n*	**I + II**	**I:II**
Me	1	(86)	88:12
MeO	1	(76)	91:9
Me	2	(95)	55:45
Et	2	(94)	57:43
t-Bu	2	(0)	—
Ph	2	(92)	95:5

49



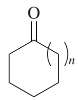
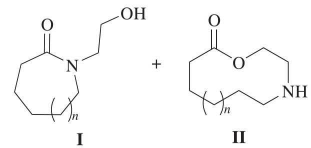
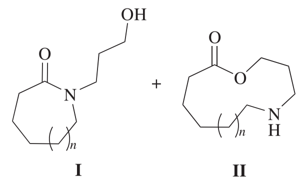
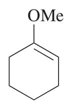
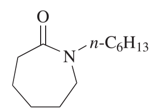
n-$C_6H_{13}N_3$, $TiCl_4$, CH_2Cl_2, rt, 16 h



R	
H	(80)
t-Bu	(63)
Ph	(48)

85

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-12} 	1. N_3(CH$_2$)$_2$OH, BF_3•OEt_2, CH_2Cl_2 2. Base	 I + II (see table below)	48
	1. N_3(CH$_2$)$_3$OH, BF_3•OEt_2, CH_2Cl_2 2. Base	 I + II (see table below)	48
C_7 	1. n-$C_6H_{13}N_3$, TfOH, CH_2Cl_2 2. NaI, acetone	 (27)	94

First entry (N_3(CH$_2$)$_2$OH):

Base	n	I	II
KOH	1	(96)	(0)
$NaHCO_3$	1	(97)	(0)
KOH	2	(68)	(0)
$NaHCO_3$	2	(27)	(43)
KOH	3	(29)	(0)
KOH	4	(88)	(0)
$NaHCO_3$	4	(26)	(64)
KOH	5	(51)	(19)
$NaHCO_3$	5	(30)	(64)
KOH	7	(50)	(30)
$NaHCO_3$	7	(8)	(79)

Second entry (N_3(CH$_2$)$_3$OH):

Base	n	I	II
KOH	1	(95)	(0)
$NaHCO_3$	1	(91)	(0)
KOH	2	(99)	(0)
$NaHCO_3$	2	(21)	(70)
KOH	3	(3)	(28)
KOH	4	(23)	(40)
$NaHCO_3$	4	(46)	(49)
KOH	5	(25)	(54)
$NaHCO_3$	5	(29)	(67)
KOH	7	(36)	(45)
$NaHCO_3$	7	(5)	(93)

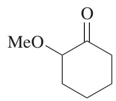
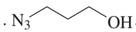
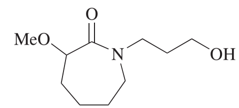
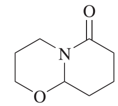
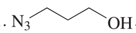
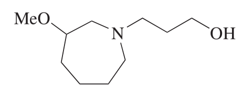
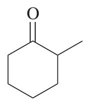
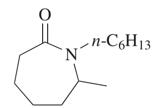
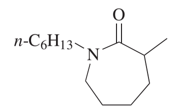
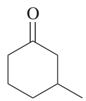
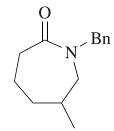
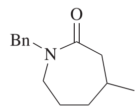
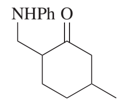
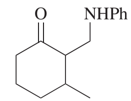
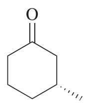
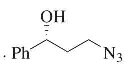
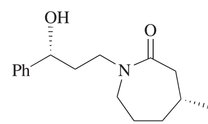
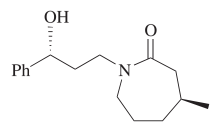
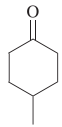
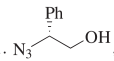
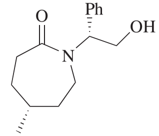
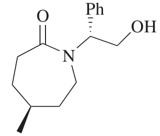
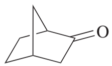
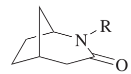
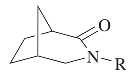
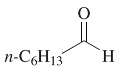
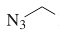
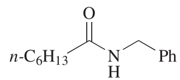
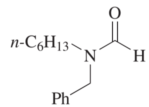
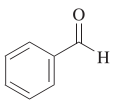
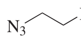
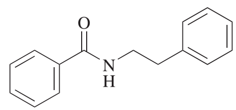
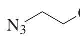
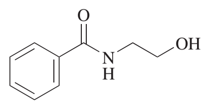
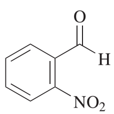
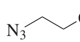
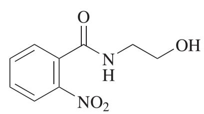
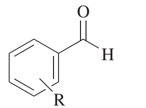
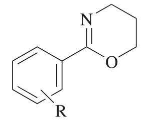
	1. , BF_3•OEt_2, CH_2Cl_2, 0° to reflux, 48 h 2. KOH	 (61) +  (7)	49
	1. , BF_3•OEt_2, CH_2Cl_2, 0° to reflux, 48 h 2. $NaBH_4$	 (64)	46
	n-$C_6H_{13}N_3$, $TiCl_4$, CH_2Cl_2, rt, 16 h	 **I** +  **II** **I + II** (5–19), **I:II** = 1.7:1	22
	BnN_3, $TiCl_4$, CH_2Cl_2, rt, 16 h	 **I** +  **II** +  **III** +  **IV** **I + II** (44), **III + IV** (11)	85
	1. , BF_3•OEt_2, CH_2Cl_2, –82° to rt, 48 h 2. KOH	 **I** +  **II** **I + II** (90), **I:II** = 98:2	99

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	1. , BF_3•OEt_2, *n*-pentane, –20°, 23 h 2. KOH	 (78) +  (22)	98
	RN_3, $TiCl_4$, CH_2Cl_2, rt, 16 h	 I +  II R / I + II / I:II *n*-C_6H_{13} / (40) / 1:5 Bn / (46) / 1:2	22
	Ph, promoter, 17–19 h	 I +  II Promoter / I / II TFA / trace / trace $TiCl_4$ / (16) / (10)	632
	Ph, H_2SO_4, 75°	 (10)	21
	OH, H_2SO_4, 75°	 (—)	21
	OH, H_2SO_4, 80°, 15 min	 (63)	21

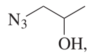


H_2SO_4, PhH, reflux

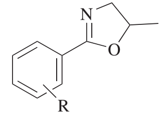


R	
4-O_2N	(70)
3-O_2N	(82)

45



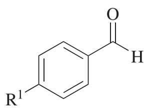
H_2SO_4, PhH, reflux

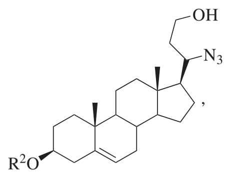


R	
4-O_2N	(53)
3-O_2N	(56)

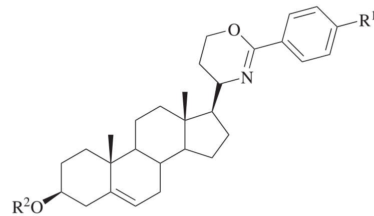
45

C_{7-8}





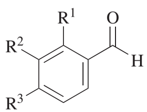
$BF_3{\bullet}OEt_2$, CH_2Cl_2, 0°, 2 h

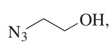


R^1	R^2	
H	H	(65)
H	Ac	(65)
Cl	H	(87)
Cl	Ac	(60)
Br	H	(82)
Br	Ac	(83)
O_2N	H	(92)
O_2N	Ac	(75)
MeO	H	(78)
MeO	Ac	(78)

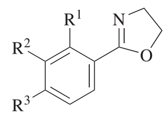
633

C_{7-9}





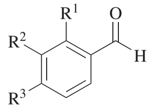
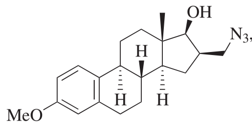
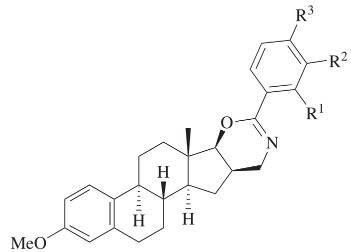
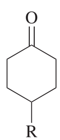
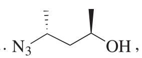
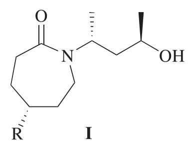
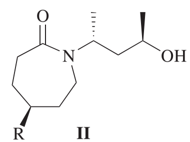
H_2SO_4, PhH, reflux



R^1	R^2	R^3	
H	H	H	(77)
HO	H	H	(15)
H	H	HO	(25)
Cl	H	Cl	trace
H	H	Cl	(75)
H	H	O_2N	(70)
H	O_2N	H	(73)
H	H	Me_2N	(10)

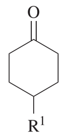
21

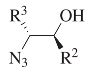
TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

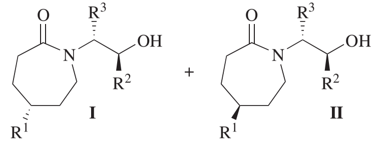
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-9} 	 BF_3•OEt_2, CH_2Cl_2, 0° to rt, 1 h	 (see table below)	630
C_{7-10} 	1.  , BF_3•OEt_2, CH_2Cl_2 2. KOH	 **I** +  **II** (see table below)	98

R^1	R^2	R^3	
H	H	H	(82)
H	H	F	(82)
H	H	HO	(30)
H	H	O_2N	(92)
H	O_2N	H	(65)
O_2N	H	H	(30)
H	H	Cl	(88)
H	Cl	H	(62)
Cl	H	H	(26)
H	H	Br	(78)
H	H	Me	(30)
H	H	NC–	(59)
H	H	CHO	(49)
H	H	MeO	(73)
H	H	Me_2N	(22)
H	H	AcO	(87)

R	**I + II**	**I:II**
Me	(98)	59:41
t-Bu	(98)	60:40



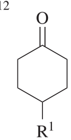


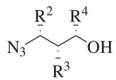


98

R^1	R^2	R^3	**I + II**	**I:II**
Me	H	Ph	(97)	78:22
Me	Ph	Ph	(51)	87:13
t-Bu	H	Ph	(83)	85:15
t-Bu	Ph	H	(73)	56:44
t-Bu	Ph	Ph	(64)	88:12

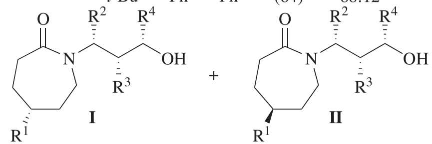
C_{7-12}



1.  ,

BF_3•OEt_2, CH_2Cl_2

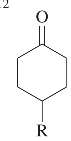
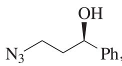
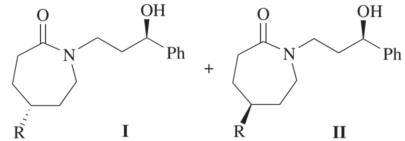
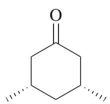
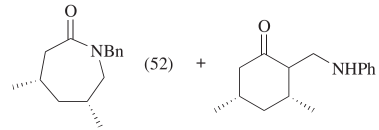
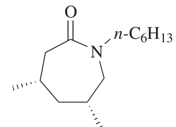
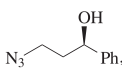
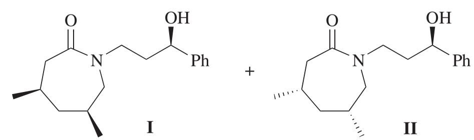
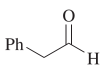
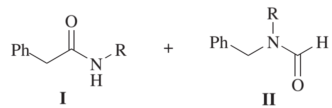
2. KOH



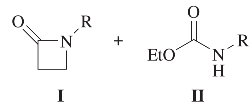
98

R^1	R^2	R^3	R^4	**I + II**	**I:II**
Me	H	Me	H	(93)	78:22
Me	Me	H	Me	(98)	98:2
Me	H	*i*-Pr	H	(88)	88:12
Me	Ph	H	H	(96)	89:11
Me	H	Ph	H	(93)	60:40
Me	H	H	Ph	(98)	93:7
t-Bu	H	Me	H	(98)	74:26
t-Bu	Me	H	Me	(94)	94:6
t-Bu	H	*i*-Pr	H	(85)	88:12
t-Bu	Ph	H	H	(94)	90:10
t-Bu	H	Ph	H	(98)	60:40
t-Bu	H	H	Ph	(100)	95:5
t-Bu	3,4,5-$(MeO)_3C_6H_2$	H	H	(94)	90:10
Ph	H	H	Ph	(99)	96:4

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-12} 	1. , $BF_3{\bullet}OEt_2$, CH_2Cl_2, –82° to rt, 48 h 2. KOH	 R | **I + II** | **I:II** Me | (98) | 93:7 *t*-Bu | (100) | 98:2 Ph | (99) | 98:2	99
C_8 	BnN_3, $TiCl_4$, CH_2Cl_2, rt, 16 h	 (52) + (35)	85
	n-$C_6H_{13}N_3$, $TiCl_4$, CH_2Cl_2, rt, 16 h	 (62)	85
	1. , $BF_3{\bullet}OEt_2$, CH_2Cl_2, –82° to rt, 48 h 2. KOH	 **I + II** (86), **I:II** = 99:1	98
	RN_3, promoter, 17–19 h		632

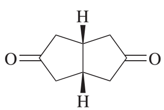
RN_3, BF_3•OEt_2, CH_2Cl_2,

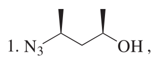


R	Promoter	**I**	**II**
n-C_6H_{13}	TFA	(19)	(13)
n-C_6H_{13}	$TiCl_4$	(29)	(26)
Bn	TFA	trace	trace
Bn	$TiCl_4$	(21)	(10)
$PhCH_2CH_2$	TFA	(16)	(16)
$PhCH_2CH_2$	$TiCl_4$	(22)	(19)

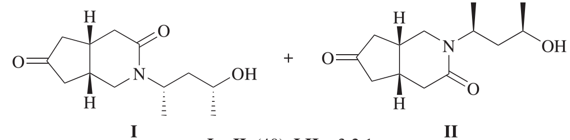
R	**I**	**II**
Bn	(45)	(13)
n-C_6H_{13}	(58)	(40)
3-$MeOC_6H_4CH_2$	(36)	(60)
4-$MeOC_6H_4CH_2$	(27)	(35)
4-$MeO_2CC_6H_4CH_2$	(38)	(43)
4-$BrC_6H_4CH_2$	(45)	(34)

634



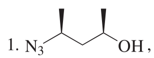


HCl, 0° to rt, 6 h
2. NaOH



I + **II** (40), **I**:**II** = 3.2:1

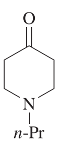
116

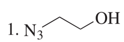


BF_3•OEt_2, CH_2Cl_2, 0° to rt
2. $NaHCO_3$

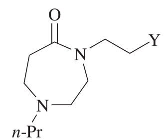
I + **II** (40), **I**:**II** = 2:1

116





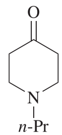
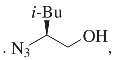
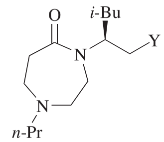
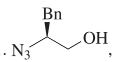
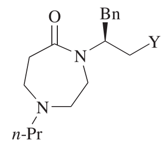
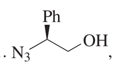
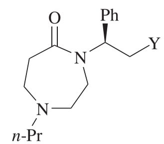
BF_3•OEt_2, CH_2Cl_2,
0° to rt, 12 h
2. NaY, DMF, 70°, 24 h

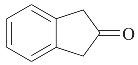
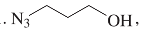
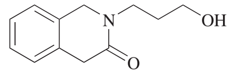
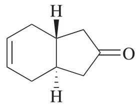
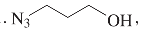
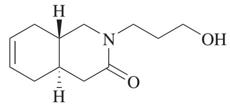
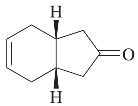
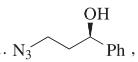
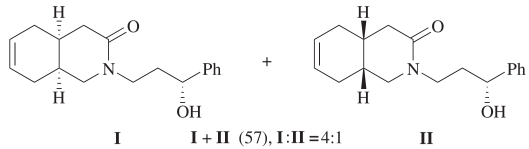
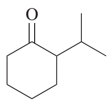
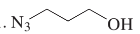
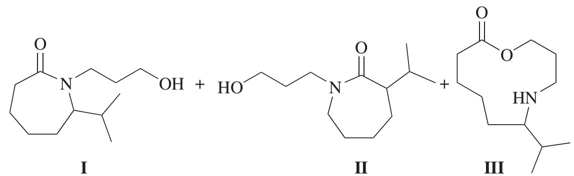
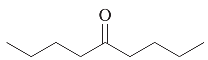
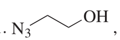
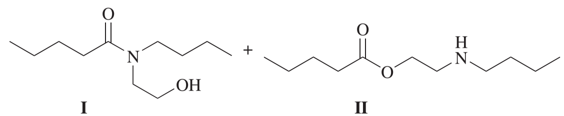


Y	
N_3	(24)
NC–	(28)
PhO	(40)
PhS	(4)
4-BrC_6H_4S	(40)
4-MeC_6H_4S	(15)
4-$MeOC_6H_4S$	(28)
4-(AcNH)C_6H_4S	(34)

631

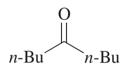
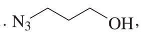
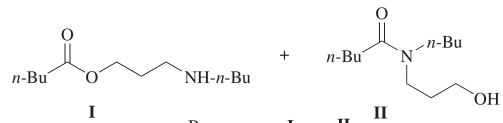
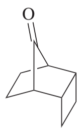
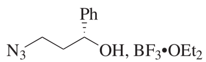
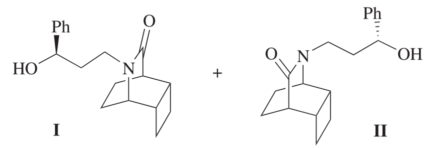
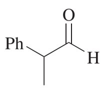
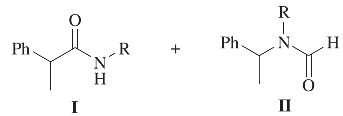
TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
C_8					
	1. , $BF_3•OEt_2$, CH_2Cl_2, 0° to rt, 12 h 2. NaY, DMF, 70°, 24 h		Y		631
			N_3	(22)	
			NC–	(33)	
			PhO	(41)	
			PhS	(12)	
			4-BrC_6H_4S	(41)	
			4-MeC_6H_4S	(17)	
			4-$MeOC_6H_4S$	(33)	
			4-(AcNH)C_6H_4S	(22)	
	1. , $BF_3•OEt_2$, CH_2Cl_2, 0° to rt, 12 h 2. NaY, DMF, 70°, 24 h		Y		631
			N_3	(35)	
			NC–	(36)	
			PhO	(37)	
			PhS	(14)	
			4-BrC_6H_4S	(37)	
			4-MeC_6H_4S	(43)	
			4-$MeOC_6H_4S$	(36)	
			4-(AcNH)C_6H_4S	(43)	
	1. , $BF_3•OEt_2$, CH_2Cl_2, 0° to rt, 12 h 2. NaY, DMF, 70°, 24 h		Y		631
			N_3	(37)	
			NC–	(26)	
			PhO	(17)	
			PhS	(22)	
			4-BrC_6H_4S	(33)	
			4-MeC_6H_4S	(24)	
			4-$MeOC_6H_4S$	(16)	
			4-(AcNH)C_6H_4S	(27)	

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	1. , BF_3•OEt_2, CH_2Cl_2, rt, 3 h 2. $NaHCO_3$, rt, 30 min	 (80)	95
	1. , BF_3•OEt_2, CH_2Cl_2, rt, 3 h 2. $NaHCO_3$, rt, 30 min	 (88)	95
	1. , BF_3•OEt_2, CH_2Cl_2, –82° to rt, 48 h 2. KOH	 **I** + **II** (57), **I**:**II** = 4:1	98
	1. , BF_3•OEt_2, CH_2Cl_2, 0° to reflux, 48 h 2. KOH	 **I** + **II** + **III** (40), **I**:**II**:**III** = 54:23:23	49
	1. , BF_3•OEt_2, CH_2Cl_2 2. Base	 **I** **II**	48

Base	I	II
KOH	(55)	(28)
$NaHCO_3$	(6)	(92)

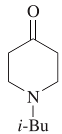
TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

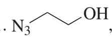
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	1.  BF_3•OEt_2, CH_2Cl_2 2. Base		48
			635
	RN_3, promoter, 17–19 h		632

Base	**I**	**II**
KOH	(64)	(18)
$NaHCO_3$	(75)	(0)

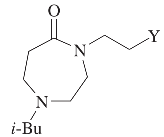
Conditions	**I + II**	**I:II**
CH_2Cl_2, 0° to rt, 1 h; reflux, 12 h	(22)	50:50
CH_2Cl_2, 0° to rt, 12 h; reflux, 5 h	(22)	56:44
CCl_4, rt, 12 h	(64)	*ca* 50:50
CCl_4, –20° to rt, 36 h	(83)	58:42

R	Promoter	**I**	**II**
n-C_6H_{13}	TFA	(23)	(8)
n-C_6H_{13}	$TiCl_4$	(35)	(27)
Bn	TFA	trace	trace
Bn	$TiCl_4$	(33)	(11)
$PhCH_2CH_2$	TFA	(13)	(5)
$PhCH_2CH_2$	$TiCl_4$	(20)	(30)



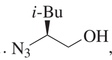
1. 

BF_3•OEt_2, CH_2Cl_2,
0° to rt, 12 h
2. NaY, DMF, 70°, 24 h

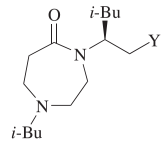


Y	
N_3	(29)
NC–	(34)
PhO	(45)
PhS	(19)
4-BrC_6H_4S	(45)
4-MeC_6H_4S	(50)
4-$MeOC_6H_4S$	(34)
4-(AcNH)C_6H_4S	(39)

631

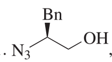
1. 

BF_3•OEt_2, CH_2Cl_2,
0° to rt, 12 h
2. NaY, DMF, 70°, 24 h

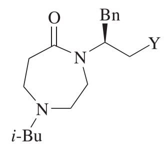


Y	
N_3	(10)
NC–	(60)
PhO	(49)
PhS	(36)
4-BrC_6H_4S	(49)
4-MeC_6H_4S	(28)
4-$MeOC_6H_4S$	(60)
4-(AcNH)C_6H_4S	(36)

631

1. 

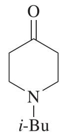
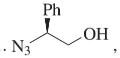
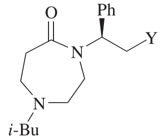
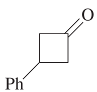
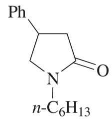
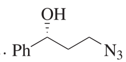
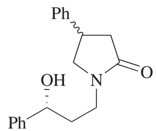
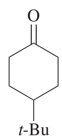
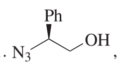
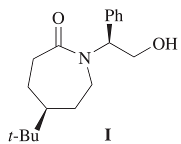
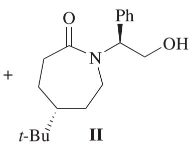
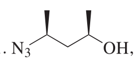
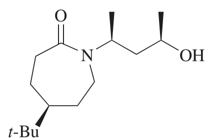
BF_3•OEt_2, CH_2Cl_2,
0° to rt, 12 h
2. NaY, DMF, 70°, 24 h

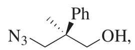


Y	
N_3	(50)
NC–	(35)
PhO	(36)
PhS	(19)
4-BrC_6H_4S	(36)
4-MeC_6H_4S	(43)
4-$MeOC_6H_4S$	(35)
4-(AcNH)C_6H_4S	(34)

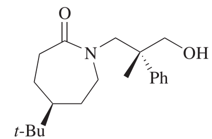
631

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

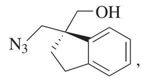
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	1. , BF_3•OEt_2, CH_2Cl_2, 0° to rt, 12 h 2. NaY, DMF, 70°, 24 h	 Y: N_3 (53); NC- (18); PhO (27); PhS (10); 4-BrC_6H_4S (12); 4-MeC_6H_4S (19); 4-$MeOC_6H_4S$ (23); 4-$(AcNH)C_6H_4S$ (21)	631
C_{10} 	n-$C_6H_{13}N_3$, $TiCl_4$, CH_2Cl_2, rt, 16 h	 (51)	85
	1. , BF_3•OEt_2, CH_2Cl_2, –82° to rt, 48 h 2. KOH	 (82)[d]	98
	1. , BF_3•OEt_2, n-pentane, –20°, 23 h 2. KOH	 I +  II **I + II** (70), **I**:**II** = 7.2:1	95
	1. , BF_3•OEt_2, CH_2Cl_2 2. KOH	 (90–94)	95



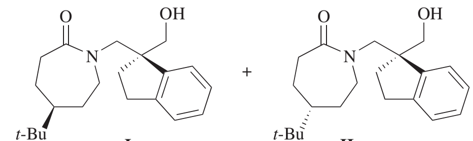
BF_3•OEt_2, CH_2Cl_2



(99) 636



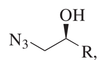
BF_3•OEt_2, CH_2Cl_2



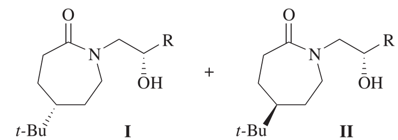
I **II**

I + II (85), **I:II** = 77:23

636



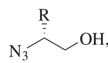
BF_3•OEt_2, CH_2Cl_2, –78°



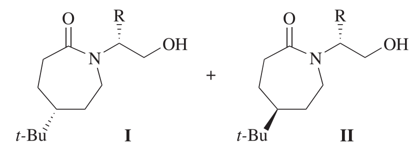
I **II**

637

R	**I + II**	**I:II**
$MeOCH_2$	(98)	97:3
c-C_6H_{11}	(91)	56:44



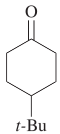
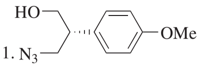
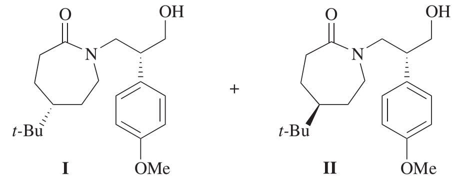
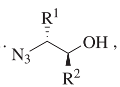
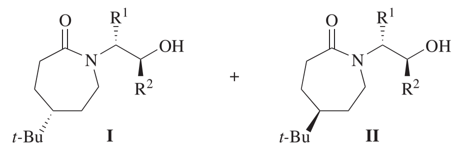
BF_3•OEt_2, CH_2Cl_2, –78°



I **II**

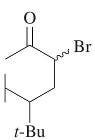
637

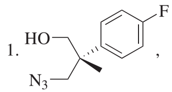
R	**I + II**	**I:II**
$MeOCH_2$	(96)	83:17
c-C_6H_{11}	(—)	75:25

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	1. , BF_3•OEt_2, –78° to rt 2. 10% aq KOH		638
	1. , BF_3•OEt_2, CH_2Cl_2, –78° to rt 2. 10% aq KOH		638

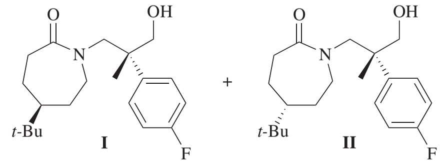
Solvent	I + II	I:II
pentane/CH_2Cl_2	(78)	47:53
toluene	(97)	47:53
Et_2O	(98)	54:47
diglyme	(99)	72:28
CH_2Cl_2	(99)	47:53

R^1	R^2	I + II	I:II
H	*c*-C_6H_{11}	(91)	56:44
c-C_6H_{11}	H	(85)	75:25
Ph	H	(89)	85:15
4-$O_2NC_6H_4$	H	(97)	66:34
3,4,5-$(MeO)_3C_6H_2$	H	(96)	86:14



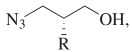


BF$_3$•OEt$_2$, CH$_2$Cl$_2$, –78° to rt
2. 10% aq KOH

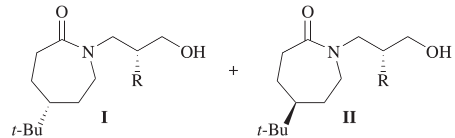


I + II (93), I:II = 93:7

638

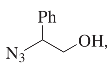


BF$_3$•OEt$_2$, CH$_2$Cl$_2$

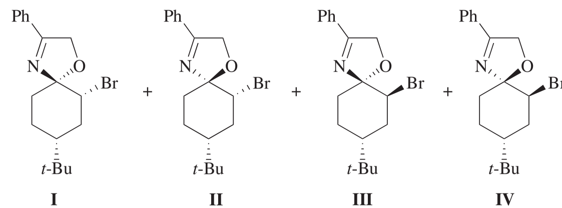


R	I + II	I:II
Me	(—)	74:26
i-Pr	(—)	88:12
Ph	(85)	64:36
4-FC$_6$H$_4$	(73)	69:31
4-O$_2$NC$_6$H$_4$	(86)	76:24
4-BrC$_6$H$_4$	(90)	68:32
4-MeOC$_6$H$_4$	(99)	47:53
3,4,5-(MeO)$_3$C$_6$H$_2$	(99)	43:57

636



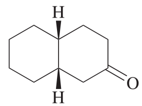
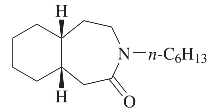
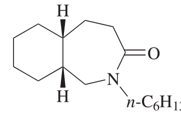
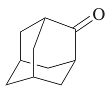
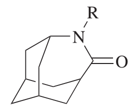
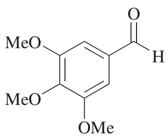
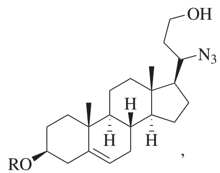
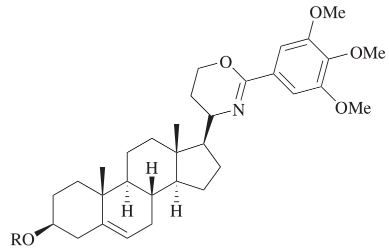
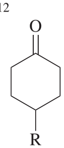
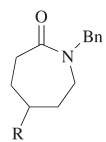
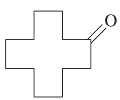
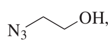
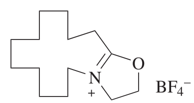
BF$_3$•OEt$_2$, CH$_2$Cl$_2$

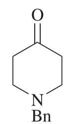


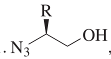
I + II + III + IV (47), I:II:III:IV = —

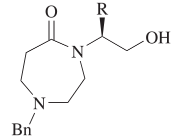
98

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	n-$C_6H_{13}N_3$, $TiCl_4$, CH_2Cl_2, rt, 16 h	 (25) +  (25)	85
	RN_3, $TiCl_4$, CH_2Cl_2, rt, 16 h	 R: n-C_6H_{13} (100); Bn (98)	85
	, BF_3•OEt_2, CH_2Cl_2, 0°, 2 h	 R: H (65); Ac (80)	633
$C_{10–12}$ 	BnN_3, $TiCl_4$, CH_2Cl_2, rt, 16 h	 R: t-Bu (65); Ph (70)	85
C_{12} 	, BF_3•OEt_2, CH_2Cl_2, –5°, 3 h; reflux, 192 h	 (90)	639

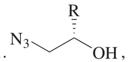


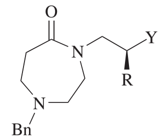
1. , $BF_3•OEt_2$, CH_2Cl_2, 0° to rt
2. $NaHCO_3$



R	
H	(79)
i-Bu	(76)
Ph	(64)
Bn	(85)

631

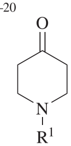
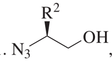
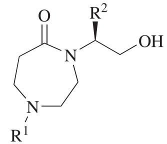
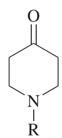
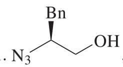
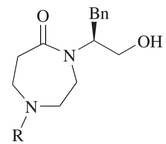
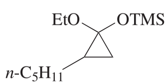
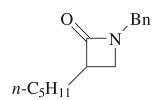
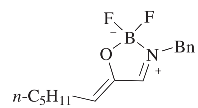
1. , $BF_3•OEt_2$, CH_2Cl_2, 0° to rt
2. NaY, DMF, 70°



R	Y	
H	N_3	(81)
H	PhO	(67)
H	PhS	(80)
H	NC–	(79)
i-Pr	N_3	(60)
i-Pr	PhO	(55)
i-Pr	PhS	(58)
i-Pr	NC–	(63)
i-Bu	N_3	(66)
i-Bu	PhO	(63)
i-Bu	PhS	(62)
i-Bu	NC–	(69)
Ph	N_3	(74)
Ph	PhO	(62)
Ph	PhS	(70)
Ph	NC–	(70)
Bn	N_3	(66)
Bn	PhO	(58)
Bn	PhS	(60)
Bn	NC–	(74)
4-$BnOC_6H_4CH_2$	N_3	(55)
4-$BnOC_6H_4CH_2$	PhO	(40)
4-$BnOC_6H_4CH_2$	PhS	(52)
4-$BnOC_6H_4CH_2$	NC–	(52)

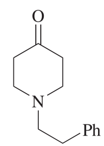
640

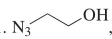
TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-20} 	1. , BF_3•OEt_2, TfOH, CH_2Cl_2 2. KOH, aq $NaHCO_3$		641
	1. , promoter 2. KOH		641
C_{13} 	BnN_3, BF_3•OEt_2, CH_2Cl_2, MW, 135°, 10 min	 (12) +  (5)	634

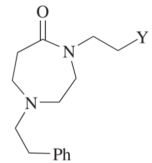
R^1	R^2	
Bn	*i*-Pr	(89)
Bn	*i*-Bu	(87)
Bn	4-$BnOC_6H_4CH_2$	(63)
Bn	$CbzNH(CH_2)_3$	(84)
Bn	$CbzNH(CH_2)_4$	(88)
Bn	$MeS(CH_2)_2$	(55)
Bn	BnO_2C	(62)
Cbz	*i*-Bu	(52)
$CbzNHCH_2CO$	*i*-Bu	(79)
Fmoc	*i*-Pr	(63)
Fmoc	*i*-Bu	(68)

R	Promoter	
Bn	BF_3•OEt_2	(52)
Bn	TfOH	(84)
Cbz	BF_3•OEt_2	(46)
Cbz	TfOH	(51)
Fmoc	BF_3•OEt_2	(74)
Fmoc	TfOH	(55)

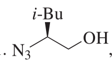


1. 

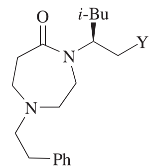
,
BF$_3$•OEt$_2$, CH$_2$Cl$_2$,
0° to rt, 12 h
2. NaY, DMF, 70°, 24 h



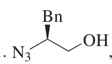
Y		
N_3	(32)	
NC–	(29)	631
PhO	(32)	
PhS	(18)	
4-BrC$_6$H$_4$S	(42)	
4-MeC$_6$H$_4$S	(41)	
4-MeOC$_6$H$_4$S	(29)	
4-(AcNH)C$_6$H$_4$S	(18)	

1. 

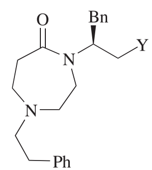
,
BF$_3$•OEt$_2$, CH$_2$Cl$_2$,
0° to rt, 12 h
2. NaY, DMF, 70°, 24 h



Y		
N_3	(8)	
NC–	(28)	631
PhO	(33)	
PhS	(20)	
4-BrC$_6$H$_4$S	(23)	
4-MeC$_6$H$_4$S	(29)	
4-MeOC$_6$H$_4$S	(18)	
4-(AcNH)C$_6$H$_4$S	(20)	

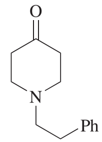
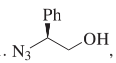
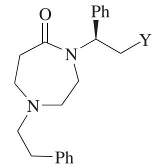
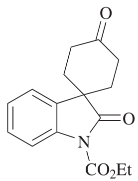
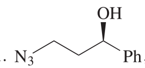
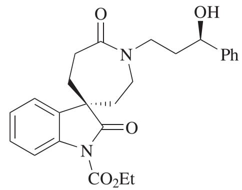
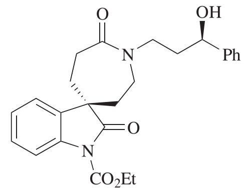
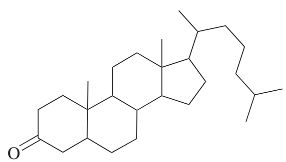
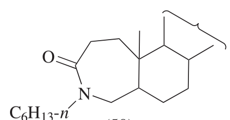
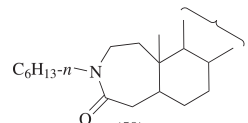
1. 

,
BF$_3$•OEt$_2$, CH$_2$Cl$_2$,
0° to rt, 12 h
2. NaY, DMF, 70°, 24 h



Y		
N_3	(41)	
NC–	(22)	631
PhO	(30)	
PhS	(12)	
4-BrC$_6$H$_4$S	(26)	
4-MeC$_6$H$_4$S	(42)	
4-MeOC$_6$H$_4$S	(22)	
4-(AcNH)C$_6$H$_4$S	(42)	

TABLE 9. SCHMIDT REACTIONS OF ALDEHYDES AND KETONES WITH ALKYL AZIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	, BF_3•OEt_2, CH_2Cl_2, 0° to rt, 12 h 2. NaY, DMF, 70°, 24 h	 Y: N_3 (23); NC– (17); PhO (4); PhS (8); 4-BrC_6H_4S (7); 4-MeC_6H_4S (20); 4-$MeOC_6H_4S$ (17); 4-$(AcNH)C_6H_4S$ (13)	631
C_{16} 	1. , BF_3•OEt_2, CH_2Cl_2, –80° to rt 2. $NaHCO_3$	 **I** +  **II** **I** + **II** (98), **I**:**II** = 87:13	476
C_{27} 	n-$C_6H_{13}N_3$, $TiCl_4$, CH_2Cl_2, rt, 16 h	 (50) +  (50)	85[e]

[a] The ratios were calculated on the basis of ^{1}H NMR integrations of the crude reaction mixtures and were normalized to 100 with the recovered azide.

[b] Yields were obtained from reactions run on a Bodan Miniblock XT automated synthesizer.

[c] Yields were obtained from reactions run on a Chemspeed SLT100 automated synthesizer.

[d] The ratio of the two diastereomers was 65:35. The stereochemistry was not determined.

[e] The stereochemistry of the substrate was not specified in the reference.

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS

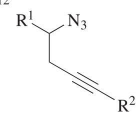
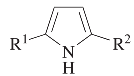
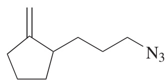
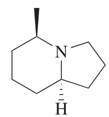
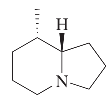
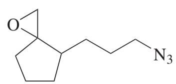
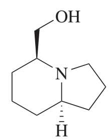
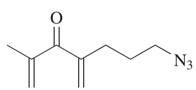
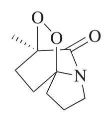
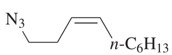
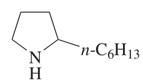
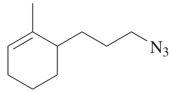
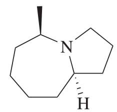
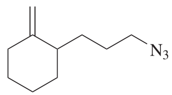
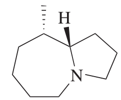
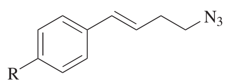
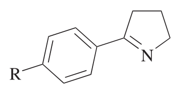
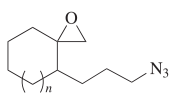
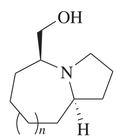
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-12} 	$(dppm)Au_2Cl_2$ (2.5 mol %), $AgSbF_6$ (5 mol %), CH_2Cl_2, 35°	 R^1 / R^2 H / *n*-Bu (76) H / 2-C_4H_3O (61) H / Ph (68) H / 4-IC_6H_4 (87) H / 2-$MeOC_6H_4$ (88) H / 3-$CF_3C_6H_4$ (93) *n*-Bu / *n*-Bu (82)	105
C_9 	1. TfOH, PhH 2. $NaBH_4$, MeOH	 **I** +  **II** **I** + **II** (71), **I**:**II** = 1:1	51
	1. Promoter, CH_2Cl_2 2. $NaBH_4$	 Promoter / Temp (°) TfOH / –40 (25) TMSOTf / –78 (21) BF_3•OEt_2 / –78 (50) $TiCl_4$ / –25 (43) $EtAlCl_2$ / –78 (63)	104
	BF_3•OEt_2, air, –78 to 0°	 (69)	642
C_{10} 	1. $Hg(ClO_4)_2$•$3H_2O$, THF 2. $NaBH_4$	 (37)	50

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	1. $Hg(ClO_4)_2$•$3H_2O$, CH_2Cl_2 2. $NaBH_4$	 (31)	50
	1. $Hg(OTf)_2$, THF 2. $NaBH_4$	**I** (45)	50
	1. TfOH, CH_2Cl_2 2. $NaBH_4$	**I** +  **II** **I** + **II** (79), **I**:**II** = 1:1	51
	1. $Hg(OTf)_2$, CH_2Cl_2 2. $NaBH_4$	**I** (87)	50
	1. $Hg(ClO_4)_2$•$3H_2O$, CH_2Cl_2 2. $NaBH_4$	**I** (84)	50
C_{10-11} 	1. TfOH, CH_2Cl_2, 0°, 30 min 2. Et_3N, rt, 15 min	 R — H (48); Cl (50); Br (40); Me (62); MeO (72)	643
	1. Et_2AlCl, CH_2Cl_2, –78°, 45 min 2. $NaBH_4$	 *n* — 1 (42); 2 (47)	644

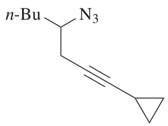
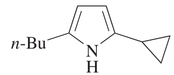
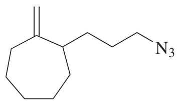
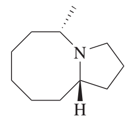
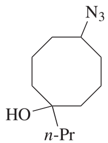
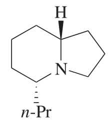
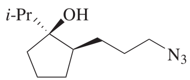
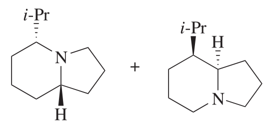
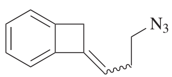
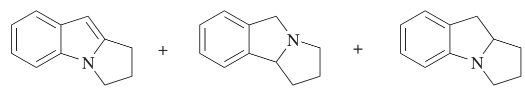
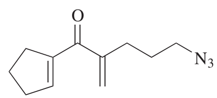
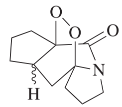
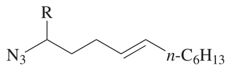
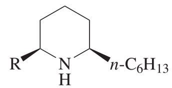
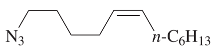
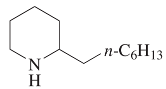
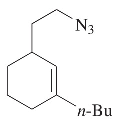
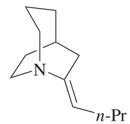
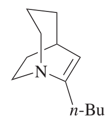
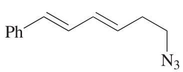
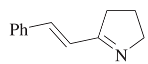
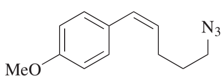
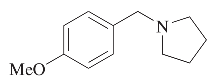
C_{11}			
	(dppm)Au_2Cl_2 (2.5 mol %), $AgSbF_3$ (5 mol %), CH_2Cl_2, 35°	 (78)	105
	1. $Hg(ClO_4)_2$•$3H_2O$, THF 2. $NaBH_4$	 (31)	50
	1. TfOH, Tf_2O, PhH 2. $NaBH_4$	 (47)	51
	1. TfOH, PhH 2. BH_3•SMe_2	 **I** **II** **I** + **II** (35), **I**:**II** = 1.3:1	51
	1. TfOH, PhH 2. $NaBH_4$	 **I** **II** **III** **I** + **II** + **III** (48), **I**:**II**:**III** = 3:1.3:1	102
	1. TfOH, PhH 2. BH_3•SMe_2	**II** + **III** (49), **II**:**III** = 1:1.5	102
	1. $Hg(OTf)_2$ 2. BH_3•SMe_2	**I** + **II** (50), **I**:**III** = 1.5:1	50

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	BF_3•OEt_2, air, –78 to 0°	 (60) dr = 2:1	642
C_{11-13} 	1. $Hg(ClO_4)_2$•$3H_2O$, THF 2. $NaBH_4$	 R / H (58) / Et (44)	50
C_{12} 	1. $Hg(ClO_4)_2$•$3H_2O$, THF 2. $NaBH_4$	 (73)	50
	1. TfOH, PhH 2. NaOH	 **I** +  **II** **I** + **II** (37), **I**:**II** = 1.1:1	51
	1. TfOH, CH_2Cl_2, 0°, 30 min 2. Et_3N, rt, 15 min	 (30)	643
	1. $Hg(ClO_4)_2$•$3H_2O$, THF 2. $NaBH_4$	 (43)	50

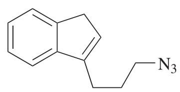
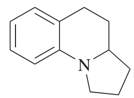
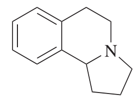
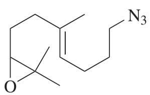
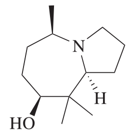
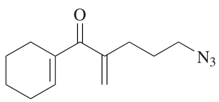
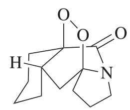
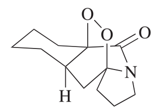
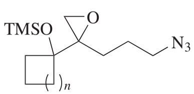
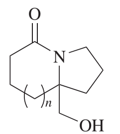
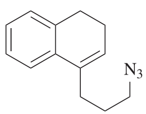
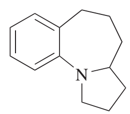
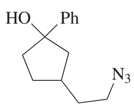
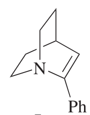
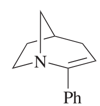
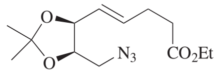
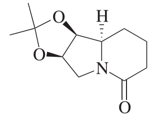
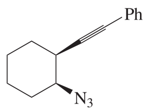
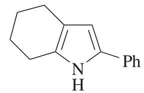
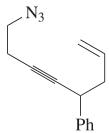
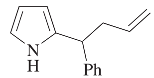
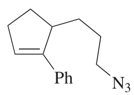
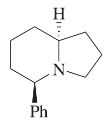
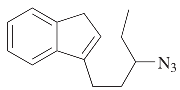
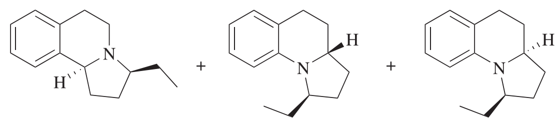
	1. TfOH, PhH 2. $NaBH_4$	 **I** +  **II**	**I** + **II** (92), **I**:**II** = 2.3:1	102
	1. Et_2AlCl, CH_2Cl_2, –78°, 45 min 2. $NaBH_4$		(36)	104
	BF_3•OEt_2, air, –78 to 0°	 **I** +  **II**	**I** + **II** (60), **I**:**II** = 2:1	642
$C_{12–14}$				
	$TiCl_4$, CH_2Cl_2, –78° to rt		*n* 1 (77); 2 (67); 3 (66)	645
C_{13}				
	1. TfOH, PhH 2. $NaBH_4$		(72)	102
	1. TfOH, PhH 2. $NaBH_4$, MeOH	 **I** +  **II**	**I** + **II** (76), **I**:**II** = 1.8:1	51

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	1. $Hg(ClO_4)_2•3H_2O$, THF 2. $NaBH_4$	 (34)	50
C_{14}			
	$(dppm)Au_2Cl_2$ (2.5 mol %), $AgSbF_6$ (5 mol %), CH_2Cl_2, 35°	 (73)	105
	$(dppm)Au_2Cl_2$ (2.5 mol %), $AgSbF_6$ (5 mol %), CH_2Cl_2, 35°	 (41)	105
	1. TfOH, PhH, 15°, 5 min 2. $NaBH_4$, MeOH, 0° to rt, 24h	 (57)	101
	1. TfOH, PhH 2. $NaBH_4$	 **I** + **II** + **III** **I + II + III** (72), **I**:**II**:**III** = 2:1:1	102

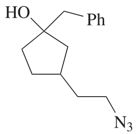
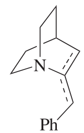
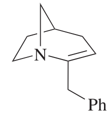
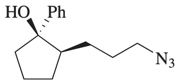
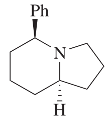
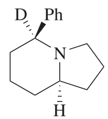
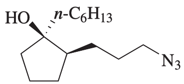
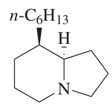
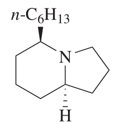
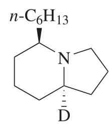
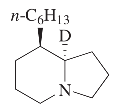
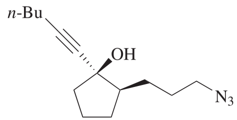
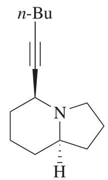
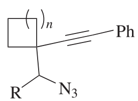
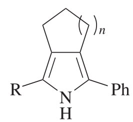
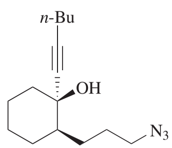
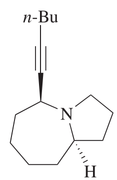
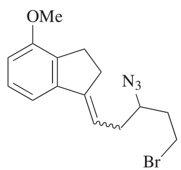
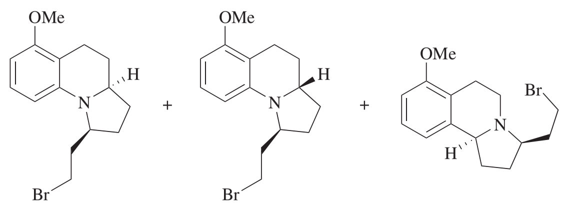
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. TfOH, PhH 2. NaOH	 **I** +  **II** **I** + **II** (21), **I**:**II** = 4.3:1	51
	1. TfOH, PhH 2. $NaBH_4$, EtOH	 **I** (40)	51
	1. $SnCl_4$ 2. $NaBH_4$	**I** (63)	101
	1. TfOH 2. $NaBD_4$	 (50)	101
	1. TfOH, PhH 2. $NaBH_4$, MeOH	 **I** +  **II** **I** + **II** (25), **I**:**II** = 1.4:1	17
	1. $SnCl_4$, CH_2Cl_2 2. BH_3•Me_2S	**I** + **II** (47), **I**:**II** = 1:1.7	17
	1. TfOH 2. $NaBD_4$	 **I** +  **II** **I** + **II** (25), **I**:**II** = 1.3:1	101

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	1. $SnCl_4$, CH_2Cl_2, –78°, 10 min 2. $NaBH_4$, MeOH, rt, 20 h	 (60)	101
$C_{14–21}$ 	$(dppm)Au_2Cl_2$ (2.5 mol %), $AgSbF_6$ (5 mol %), CH_2Cl_2, 35°	 R | *n* | H | 1 | (80) Ph | 2 | (84)	105
C_{15} 	1. $SnCl_4$, CH_2Cl_2, –78°, 10 min 2. $NaBH_4$, MeOH, rt, 20 h	 (44)	101
	1. TfOH, PhH 2. $NaBH_4$	 **I** **II** **III** **I + II + III** (72), **I**:**II**:**III** = 1:1:0.6	102

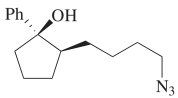
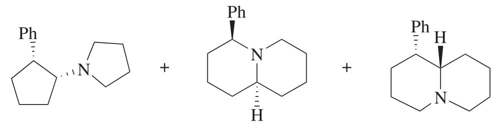
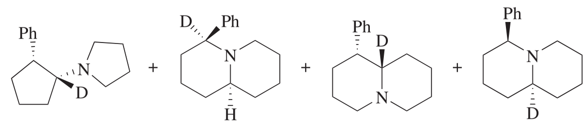
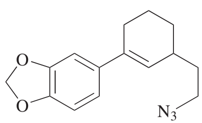
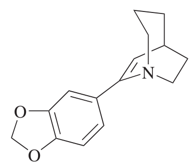
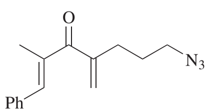
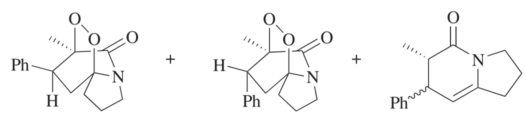
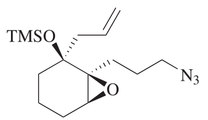
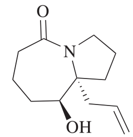
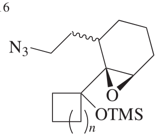
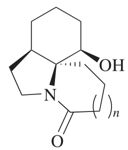
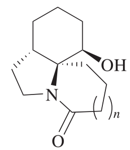
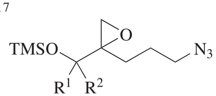
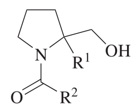
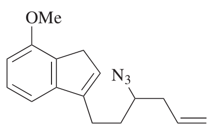
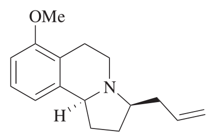
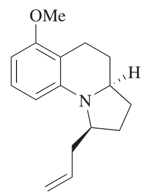
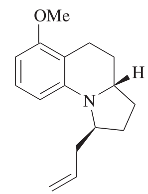
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. TfOH, PhH 2. DIBAL-H	**I** + **II** + **III** (60), **I**:**II**:**III** = 2:1:1	102
	1. TfOH, PhH 2. L-Selectride	**I** + **II** + **III** (55), **I**:**II**:**III** = 4.5:0:1	102
	1. TfOH, PhH, 15°, 5 min 2. BH_3•SMe_2, THF, rt, 14 h	 **I** **II** **III** **I** + **II** + **III** (36), **I**:**II**:**III** = 2.3:1.9:1	101
	1. TfOH, PhH, 15°, 5 min 2. $NaBD_4$, MeOD, 0°, 24 h	 **I** **II** **III** **IV** **I** + **II** + **III** + **IV** (25), **I**:**II**:**III**:**IV** = 4:3.5:2:1	101
	1. TfOH, CH_2Cl_2, 0°, 5 min 2. NaOH	 (71)	23
	BF_3•OEt_2, air, –78 to 0°	 **I** **II** **III** dr = 5:1 **I** + **II** + **III** (72), **I**:**II**:**III** = 5:5:1	642

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	$TiCl_4$, CH_2Cl_2, –78° to 0°	 (92)	645
C_{15-16} 	$TiCl_4$, CH_2Cl_2, –78° to 0°	 **I** +  **II** *n* / **I** + **II** / **I**:**II** 1 / (78) / 7:1 2 / (92) / 8:1	645
C_{15-17} 	$TiCl_4$, CH_2Cl_2, –78° to rt	 R^1 / R^2 Ph / H / (80) Ph / Me / (95) 3-$MeOC_6H_4$ / Me / (77)	645
C_{16} 	1. TfOH, PhH 2. $NaBH_4$	 **I** +  **II** +  **III** **I** + **II** + **III** (86), **I**:**II**:**III** = 4:2:1	102
	1. $Hg(OTf)_2$ 2. $NaBH_4$	**I** + **II** + **III** (45), **I**:**II**:**III** = 0:2:1	50

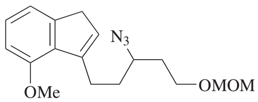
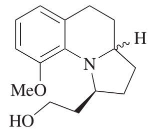
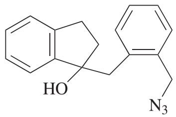
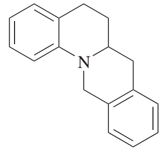
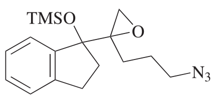
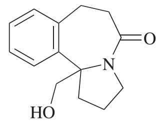
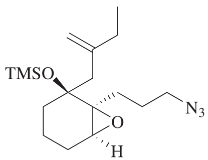
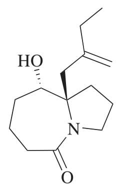
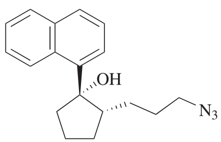
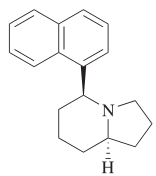
C_{17}			
	1. TfOH, PhH 2. $NaBH_4$	 (47) dr = 1.2:1	102
	1. TfOH, PhH 2. BH_3•SMe_2	 (67)	102
	$TiCl_4$, CH_2Cl_2, –78° to rt	 (61)	645
	$TiCl_4$, CH_2Cl_2, –78 to 0°	 (68)	646
C_{18}			
	1. $SnCl_4$, CH_2Cl_2, –78°, 12 min 2. BH_3•SMe_2, THF, rt, 12 h	 (68)	103

TABLE 10. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALKENES, ALKYNES, ALCOHOLS, EPOXIDES, AND OXYALLYL CATIONS (*Continued*)

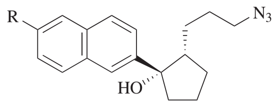
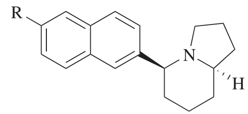
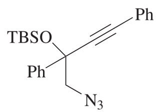
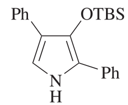
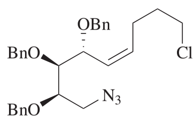
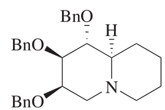
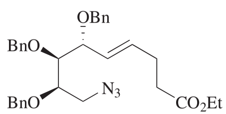
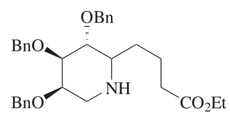
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18-19}			
	1. $SnCl_4$, CH_2Cl_2, –78°, 12 min 2. BH_3•SMe_2, THF, rt, 12 h	 R: H (60); MeO (49)	103
C_{22}			
	(dppm)Au_2Cl_2 (5 mol %), $AgSbF_6$ (10 mol %), $MeNO_2$, rt	 (58)	105
C_{30}			
	1. $Hg(OTf)_2$, THF 2. $NaBH_4$, MeOH 3. MeONa, MeOH, reflux	 (63)	50
C_{32}			
	1. $Hg(ClO_4)_2$•$3H_2O$, THF 2. $NaBH_4$, MeOH	 (41)	50

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES

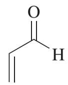
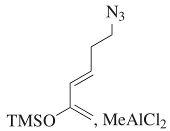
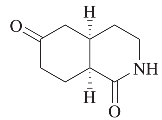
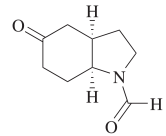
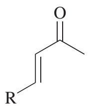
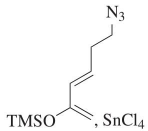
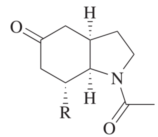
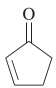
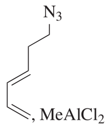
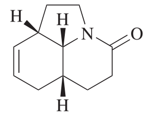
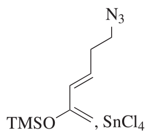
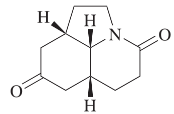
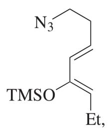
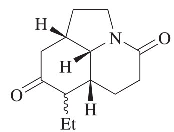
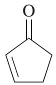
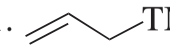
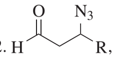
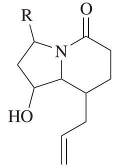
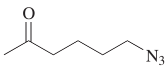
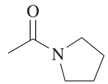
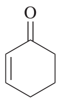
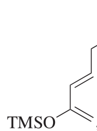
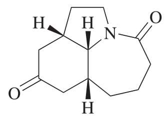
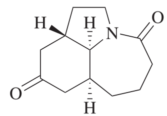
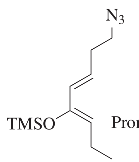
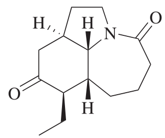
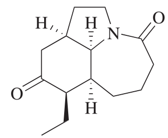
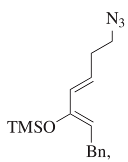
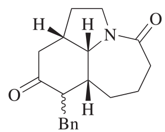
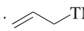
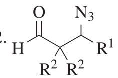
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		 (36) +  (21)	647
C_{4-5} 		 R: H (60); Me (59)	647
C_5 		 (38)	647
		 (52)	647
	 BF_3•OEt_2, CH_2Cl_2, –78° to rt	 (49)	648

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	1.  TMS, $TiCl_4$, CH_2Cl_2, –45°, 1 h 2.  R, –45°, 10 min; 0°, 6 h 3. $TiCl_4$ (2 eq), 0°, 18 h	 R: H (0); n-C_6H_{13} (0)	649
C_6 	TFA, CH_2Cl_2, rt, 16 h	 (75)	29
	, $SnCl_4$	 I +  II **I + II** (82), **I**:**II** = 3.4:1	647
	 Promoter	 I +  II Promoter / **I + II** / **I**:**II**: TMSOTf (70) 3:1; BF_3•OEt_2 (30) 0:100	650
	 Bn, BF_3•OEt_2, CH_2Cl_2, –78° to rt	 (56)	648

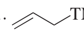
Conditions A:

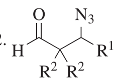
1. TMS, $TiCl_4$, CH_2Cl_2, –45°, 1 h

2. 

–45°, 10 min; 0°, 24 h

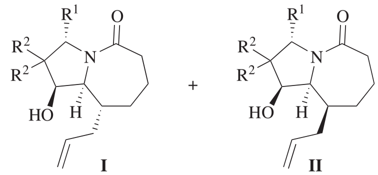
Conditions B:

1. TMS, $TiCl_4$, CH_2Cl_2, –45°, 1 h

2. 

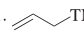
–45°, 10 min; 0°, 6 h

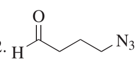
3. $TiCl_4$ (2 eq), 0°, 18 h



R^1	R^2	Conditions	**I + II**	**I:II**
H	H	A	(38)	6.4:1
H	H	B	(59)	2.6:1
H	Me	A	(42)	1:0
H	Me	B	(56)	1:0
n-C_6H_{13}	H	A	(36)	4.0:1
n-C_6H_{13}	H	B	(59)	1.8:1

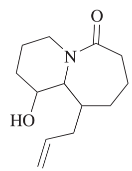
649

1. TMS, $TiCl_4$, CH_2Cl_2, –45°, 1 h

2. 

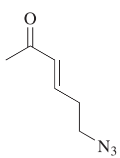
–45°, 10 min; 0°, 6 h

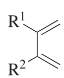
3. $TiCl_4$ (2 eq), 0°, 18 h



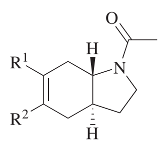
(0)

649





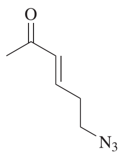
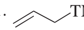
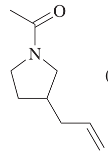
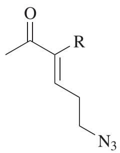
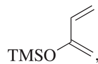
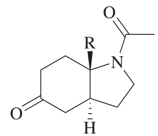
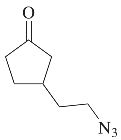
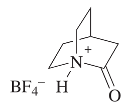
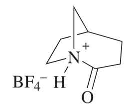
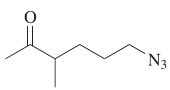
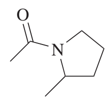
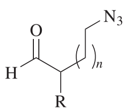
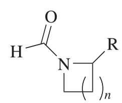
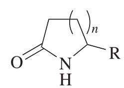
, $MeAlCl_2$



R^1	R^2	
H	H	(54)
H	Me	(73)
Me	Me	(75)

647

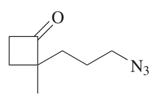
TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	1.  TMS, $TiCl_4$, CH_2Cl_2, –78°, 3 h; 0°, 5 h 2. MeOH (5 eq), rt, 45 min	 (46)	649
C_{6-7} 	 , $MeAlCl_2$	 R: H (71); Me (61)	647
C_7 	HBF_4, Et_2O, 20°	 **I** +  **II** **I** + **II** (38), **I**:**II** = 76:24	91
	TFA	 (75)	651
C_{7-13} 	Promoter, rt, 17–19 h	 **I** +  **II**	632

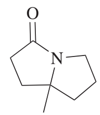
n	R	Promoter	**I**	**II**
1	allyl	TFA	(—)	(63)
1	allyl	$TiCl_4$	(—)	(90)
2	allyl	TFA	(60)	(—)
2	allyl	$TiCl_4$	(96)	(—)
3	allyl	TFA	(53)	(—)
3	allyl	$TiCl_4$	(41)	(—)
1	Bn	TFA	(—)	(77)
1	Bn	$TiCl_4$	(—)	(94)
2	Bn	TFA	(68)	(—)
2	Bn	$TiCl_4$	(85)	(—)
3	Bn	TFA	(71)	(—)
3	Bn	$TiCl_4$	(49)	(—)

248

C_8

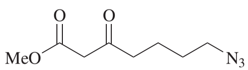


TFA, CH_2Cl_2, rt

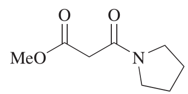


(66)

29

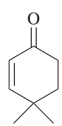


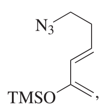
Promoter, CH_2Cl_2, rt



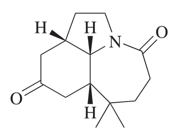
Promoter	Time	
TFA	12 h	(66)
$TiCl_4$	15 min	(64)

3





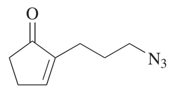
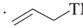
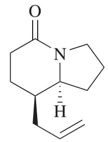
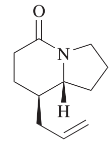
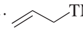
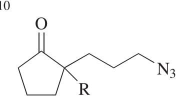
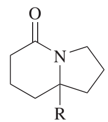
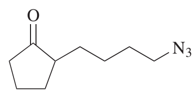
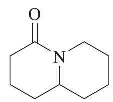
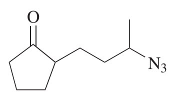
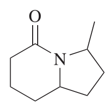
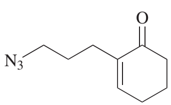
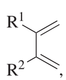
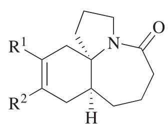
BF_3•OEt_2, CH_2Cl_2, –78° to rt



(25)

648

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	1. TMS, $TiCl_4$, CH_2Cl_2, –78°, 3 h; 0°, 5 h 2. *t*-BuOH (5 eq), rt, 45 min	 **I** +  **II** **I** + **II** (50), **I**:**II** = 64:36	649
	1. TMS, $TiCl_4$, CH_2Cl_2, –78°, 3 h; 0°, 5 h 2. aq NH_4Cl 3. TFA	**II** (47)	649
C_{8-10} 	Promoter, CH_2Cl_2, rt	 R / Promoter / Time H / TFA / 40 min (83) MeO_2C / TFA / 16 h (66) MeO_2C / $TiCl_4$ / 20 min (70)	3 29 3
C_9 	$TiCl_4$, CH_2Cl_2, rt, 16 h	 (56)	29
	$TiCl_4$, CH_2Cl_2, rt, 16 h	 (68)	29
	, $MeAlCl_2$	 R^1 / R^2 H / Me (84) Me / Me (85)	647

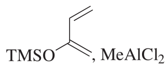
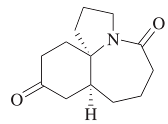
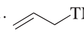
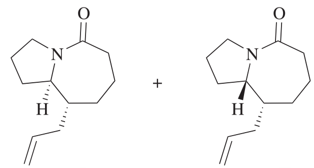
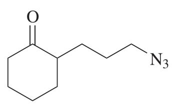
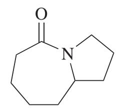
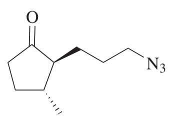
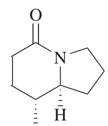
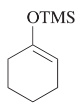
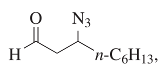
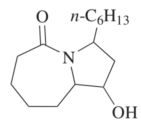
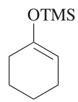
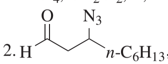
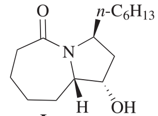
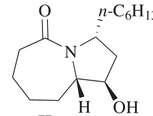
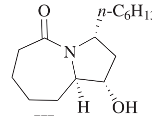
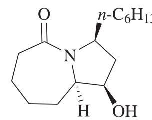
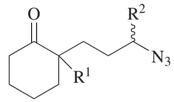
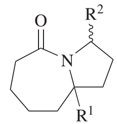
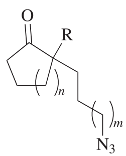
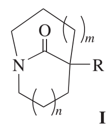
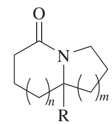
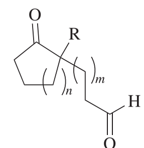
		 (91)	647
	1. TMS, $TiCl_4$, CH_2Cl_2, –78°, 3 h; 0°, 5 h 2. ROH (5 eq), rt, 45 min	 **I** + **II** ROH / **I + II** / **I:II** MeOH / (75) / 7:3 *t*-BuOH / (79) / >9:1	649
	TFA, CH_2Cl_2, rt, 3.5 h	 (85)	29
	TFA, 0°, 40 min	 (93)	111
	 $TiCl_4$, –45°, 10 min; rt, 24 h	 (27)	649

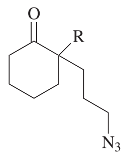
TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	1. $TiCl_4$, CH_2Cl_2, rt, 3 min 2. , –45°, 10 min; rt, 24 h	 **I** +  **II** +  **III** +  **IV** **I + II + III + IV** (56), **I**:(**II**+**III**+**IV**) = 56:44	649
C_{9-12} 	TFA, CH_2Cl_2, rt		3
C_{9-15} 	TfOH, CH_2Cl_2, 0°	 **I** +  **II** +  **III**	652

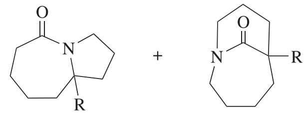
R^1	R^2	Time	
H	H	10 min	(90)
H	Me	20 min	(74)
EtO_2C	H	1 h	(93)

n	*m*	R	**I**	**II**	**III**
1	1	MeS	(0)	(43)	(0)
2	1	MeO	(23)	(52)	(0)
2	1	MeO_2C	(48)	(13)	(0)
2	1	MeS	(65)	(15)	(0)
2	2	MeS	(0)	(0)	(53)
3	1	MeS	(62)	(11)	(20)
4	1	MeS	(0)	(0)	(30)
2	1	PhS	(35)	(32)	(0)

C_{9-17}



TfOH, CH_2Cl_2, 0º



I + II

R	**I + II**	**I:II**
H	(85)	>95:5
Ph	(96)	>95:5

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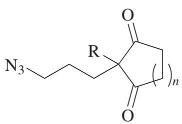
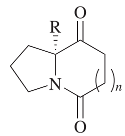


Promoter (*x* eq), rt



I

n	R	Promoter	*x*	Solvent	Time (h)	
1	Me	BF_3•OEt_2	4	Et_2O	24	(65)
1	Me	$TiCl_4$	2.5	Et_2O	1	(89)
1	Me	$EtAlCl_2$	2.5	Et_2O	6	(83)
1	Me	CuOTf	2.5	THF	72	(—)
1	Me	$ZnCl_2$	2.5	Et_2O	72	(—)
1	Me	$Yb(OTf)_3$	—	THF	72	(—)
2	Me	BF_3•OEt_2	4	Et_2O	24	(52)
2	Me	BF_3•OEt_2	2.5	Et_2O	24	(85)
2	Me	$TiCl_4$	1.1	Et_2O	1	(67)
2	Me	$EtAlCl_2$	1.1	Et_2O	24	(60)
2	Me	$EtAlCl_2$	2.5	Et_2O	6	(80)
3	Bn	$EtAlCl_2$	2.5	Et_2O	24	(87)

653

Promoter, rt, 72 h

I

n	R	Promoter	Solvent		% er
1	Me	L-menthyloxyaluminum dichloride	hexane/toluene (1:1)	(35)	0
1	Me	(*S*)-BINOLAlCl	toluene	(18)	53.0:47.0
2	Me	L-menthyloxyaluminum dichloride	hexane/toluene (1:1)	(50)	52.5:47.5
2	Me	(*S*)-BINOLAlCl	toluene	(25)	52.0:48.0
3	Bn	L-menthyloxyaluminum dichloride	hexane/toluene (1:1)	(27)	0
3	Bn	(*S*)-BINOLAlCl	toluene	(10)	0

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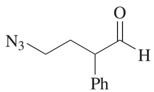
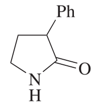
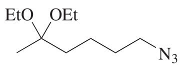
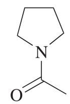
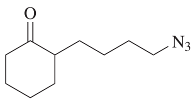
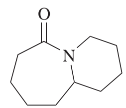
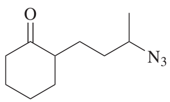
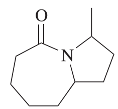
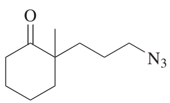
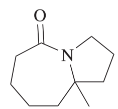
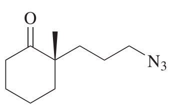
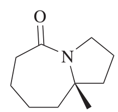
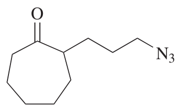
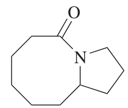
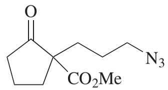
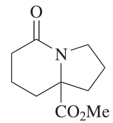
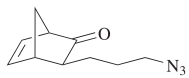
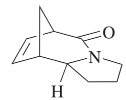
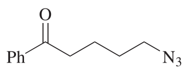
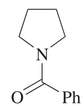
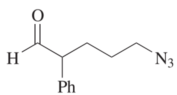
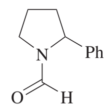
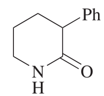
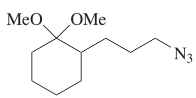
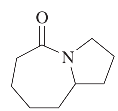
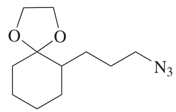
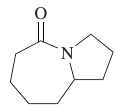
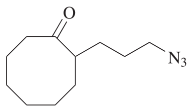
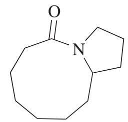
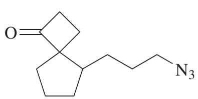
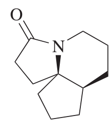
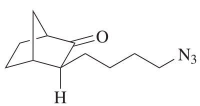
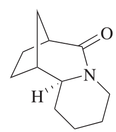
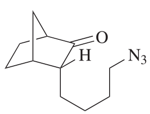
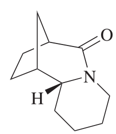
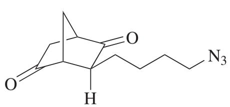
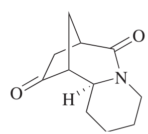
TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	TFA, CH_2Cl_2	 (29)	29
	1. TMSOTf, CH_2Cl_2, rt, 16 h 2. NaI, acetone	 (81)	94
	Promoter, CH_2Cl_2, rt, 16 h	 Promoter: TFA (0); BF_3•OEt_2 (29); $TiCl_4$ (91)	29
	TFA, CH_2Cl_2, 15 min	 (74)	29
	TFA, CH_2Cl_2, 15 min	 (87)	29
 91% ee	TFA, CH_2Cl_2, 1 h	 (87) 94.5:5.5 er	651

	TFA, CH_2Cl_2, 3 h	 (80)	29
	Promoter, CH_2Cl_2	 Promoter / Time: TFA, 16 h (66) $TiCl_4$, 30 min (70)	29
	$TiCl_4$, CH_2Cl_2, 0° to rt	 (89)	654
C_{11} 	TFA, CH_2Cl_2, rt, 16 h	 (77)	29
	Promoter, CH_2Cl_2	 **I** +  **II**	29
	1. TFA, CH_2Cl_2, rt, 16 h 2. NaI, acetone	 (72)	94

Promoter	**I**	**II**
TFA	(81)	(8)
$AlCl_3$	(69)	(8)
$SnCl_4$	(59)	(15)
$ZnCl_2$	(48)	(17)
TMSOTf	(61)	(22)

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		1. TFA, CH_2Cl_2, rt, 16 h 2. NaI, acetone	 (35)	94
		TFA, CH_2Cl_2, 16 h	 (96)	29
		$TiCl_4$, CH_2Cl_2, rt	 (39)	3
		$TiCl_4$, CH_2Cl_2	 (82)	655
		$TiCl_4$, CH_2Cl_2	 (92)	655
		$TiCl_4$, CH_2Cl_2	 (50–75)	655

C_{12}

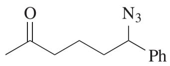
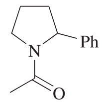
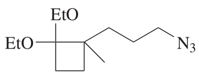
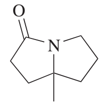
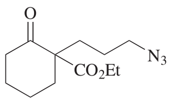
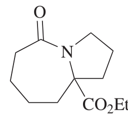
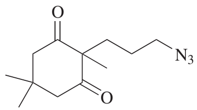
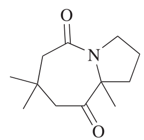
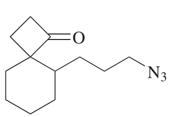
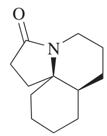
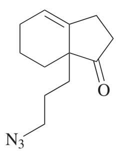
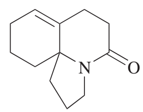
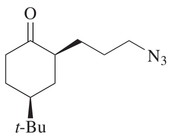
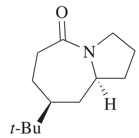
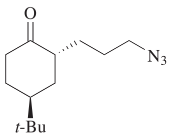
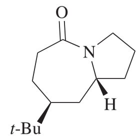
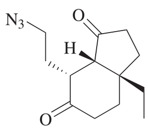
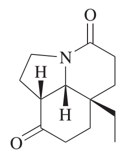
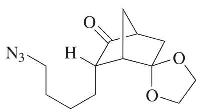
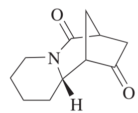
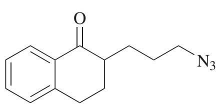
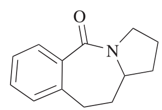
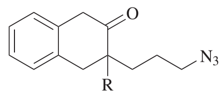
	$TiCl_4$ or TfOH, CH_2Cl_2, 0°, 15 min	 (55–58)	90
	TFA, CH_2Cl_2, rt, 16 h	 (68)	94
	TFA, CH_2Cl_2, rt, 1 h	 (93)	29
	TFA, CH_2Cl_2	 (82)	29
	$TiCl_4$, CH_2Cl_2, rt	 (81)	3
	BF_3•OEt_2, rt	 (70)	656

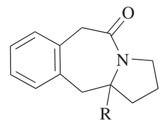
TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	TFA, CH_2Cl_2	 (96)	29
	$TiCl_4$, CH_2Cl_2	 (92)	29
	$TiCl_4$, CH_2Cl_2	 (82)	114
	$TiCl_4$, CH_2Cl_2, reflux	 (62)	115
	TfOH, CH_2Cl_2	 (45)	29

C_{13-14}



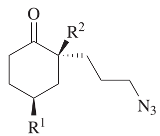
TFA, CH_2Cl_2, rt, 20 min



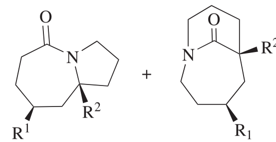
R	
H	(91)
Me	(91)

Refs.: 3

C_{13-20}



$MeAlCl_2$, CH_2Cl_2, 0°

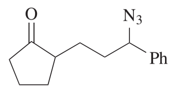


I + **II**

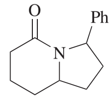
R^1	R^2	**I**	**II**
t-Bu	H	(57)	(17)
H	Ph	(96)	(—)
t-Bu	Ph	(20)	(51)
t-Bu	4-$MeOC_6H_4$	(10)	(65)

Refs.: 657

C_{14}

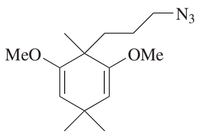


Promoter, CH_2Cl_2, 0°, 15 min

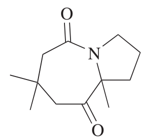


Promoter	
$TiCl_4$	(50)
TfOH	(60)

Refs.: 90

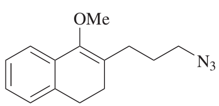


1. TfOH, CH_2Cl_2
2. NaI, acetone

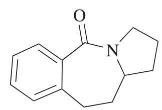


(95)

Refs.: 94



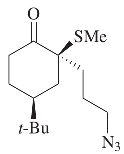
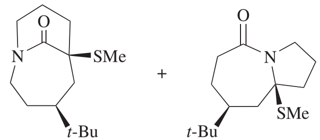
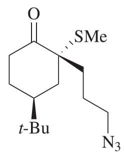
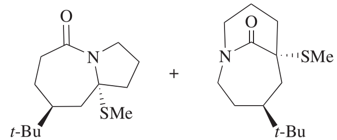
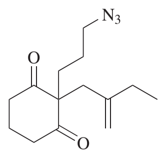
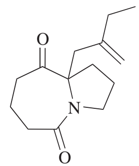
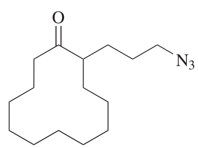
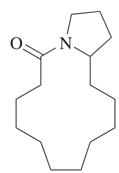
1. TFA, CH_2Cl_2
2. NaI, acetone

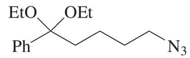
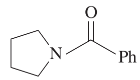
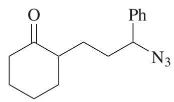
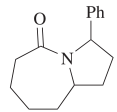
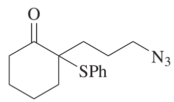
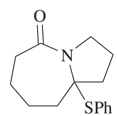
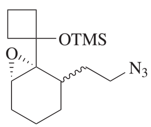
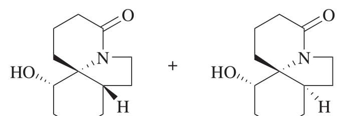
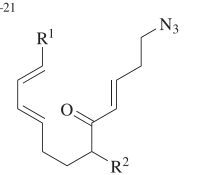
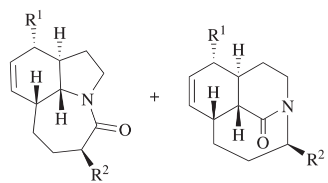


(89)

Refs.: 94

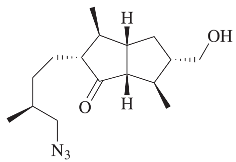
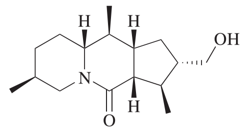
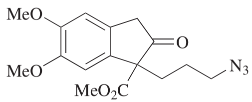
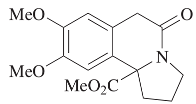
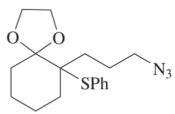
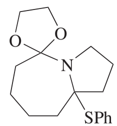
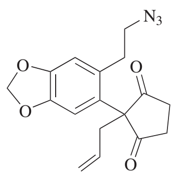
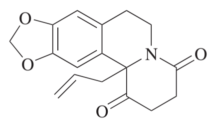
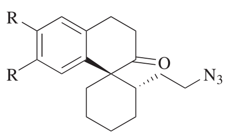
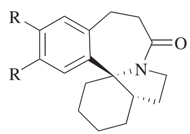
TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	TfOH, CH_2Cl_2, 0°	 **I** **II** **I + II** (74), **I**:**II** = 86:14	652
	TfOH, CH_2Cl_2, 0°	 **I** **II** **I + II** (75), **I**:**II** = >95:5	652
	$TiCl_4$, CH_2Cl_2, –78°, 15 min; rt	 (93)	658
C_{15} 	TFA, CH_2Cl_2, 2 h	 (89)	29

	1. TFA, CH_2Cl_2, rt, 16 h 2. NaI, acetone	 (79)	94
	Promoter, CH_2Cl_2, 0°, 15 min	 Promoter: TfOH (52); $TiCl_4$ (81)	90
	TfOH, CH_2Cl_2	 (42)	29
 *cis*:*trans* = 6:1	$TiCl_4$, CH_2Cl_2, –78° to rt	 **I** + **II** **I** + **II** (78), **I**:**II** = 8:1	659
$C_{15–21}$ 	$MeAlCl_2$, CH_2Cl_2, reflux, 20 h	 **I** + **II**	657

R^1	R^2	**I**	**II**
H	*i*-Pr	(43)	(28)
H	Ph	(85)	(—)
$BnO(CH_2)_2$	H	(43)	(24)

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	TfOH, CH_2Cl_2, 0°, 30 min	 (79)	660
	TfOH, CH_2Cl_2, –5° to 0°, 15 min	 (54)	661, 662
C_{17} 	TMSOTf, CH_2Cl_2, 0° to rt, 40 min	 (94)	94
	$TiCl_4$, CH_2Cl_2, 0°, 40 min	 (75)	658
$C_{17–19}$ 	TFA, CH_2Cl_2, rt, 6 h	 R: H (81); MeO (85)	110

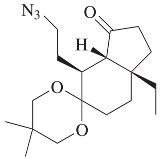
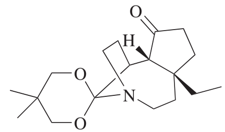
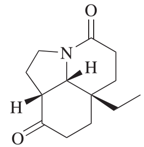
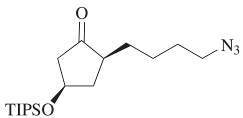
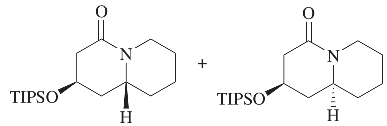
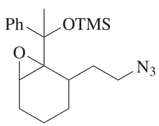
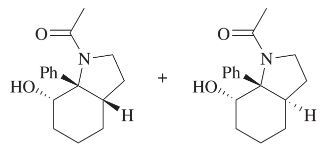
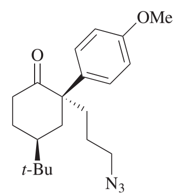
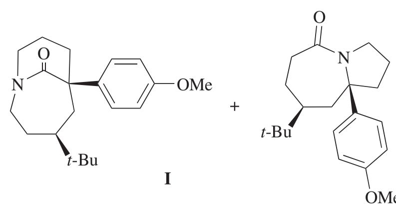
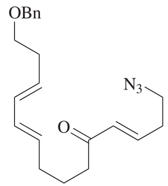
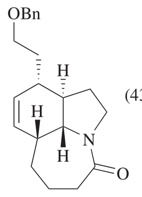
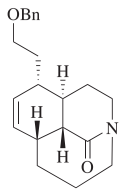
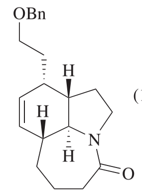
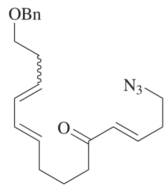
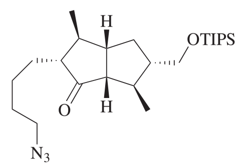
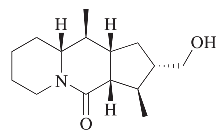
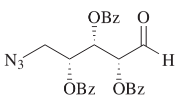
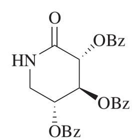
C_{18} 	$TiCl_4$, CH_2Cl_2	 (53)	114
	TFA	 (21)	114
	$TiCl_4$, CH_2Cl_2, reflux	 **I** + **II** **I + II** (79), **I:II** = 1.3:1	93
C_{19} 	$TiCl_4$, CH_2Cl_2, –78° to rt	 **I** + **II** **I + II** (80), **I:II** = 7:1	659
C_{20} 	TfOH, CH_2Cl_2, 0°	 **I** + **II** **I + II** (75), **I:II** = 87:13	652

TABLE 11. INTRAMOLECULAR SCHMIDT REACTIONS OF AZIDOALKYL ALDEHYDES AND KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21} 	Et_2AlCl, CH_2Cl_2, reflux, 18 h	 **I** (43) +  **II** (24) +  **III** (12)	92
	Promoter CH_2Cl_2, 45°	**I** + **II** + **III**	663
C_{24} 	TfOH, CH_2Cl_2, 0°, 30 min	 (52)	660
C_{26} 	$TiCl_4$, CH_2Cl_2, 0° to rt, 18 h	 (84)	664

Promoter	*x*	**I**	**II**	**III**
$InCl_3$	2.0[a]	(20)	(22)	(18)
$AlMe_3$	1.0	(0)	(0)	(0)
Et_2AlCl	1.3[a]	(28)	(20)	(12)
Et_2AlCl	1.0	(41)	(28)	(9)
$MeAlCl_2$	1.0	(43)	(24)	(12)

[a] The Promoter was added in two equal portions.

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